SPEAKER'S NOTES FROM THE HENDERSON, NV PERCHLORATE STAKEHOLDERS FORUM

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The Perchlorate Contamination Challenge: EPA's Part in Pro-Active Partnership

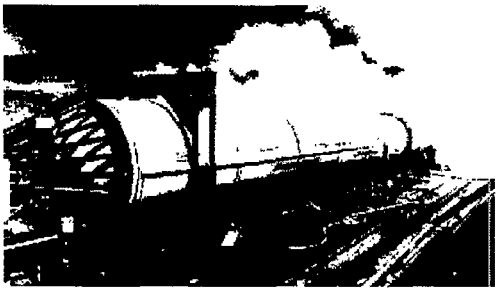
William H. Farland, Ph.D.
Director
National Center for Environmental Assessment
U.S. EPA

Perchlorate Stakeholders Forum
Sponsored by the IPSC
Henderson, NV
19-21 May 1998

I P S C

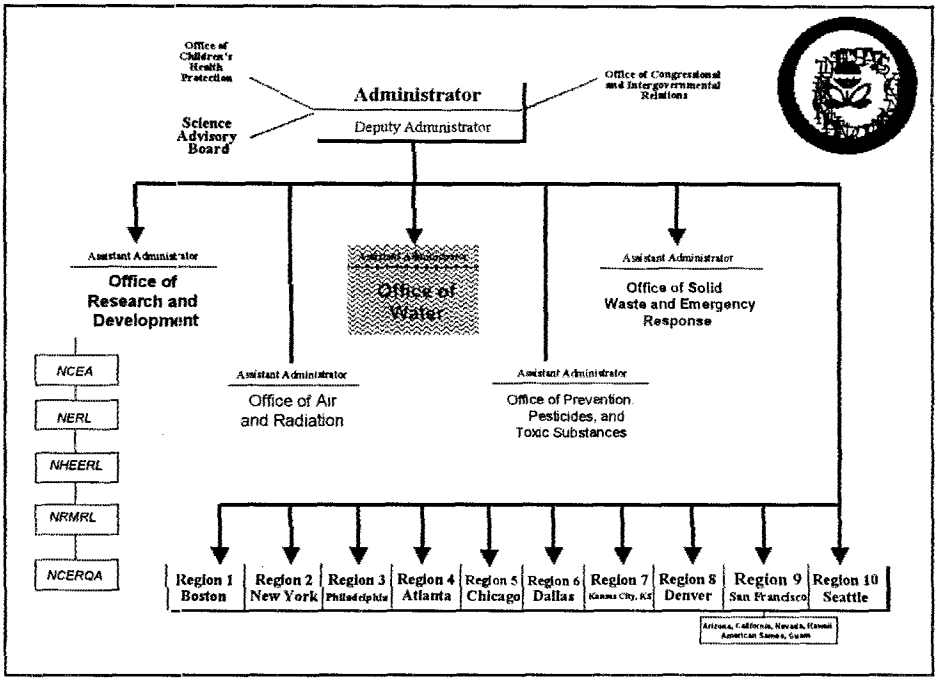
Perchlorate-tainted wells spur government action

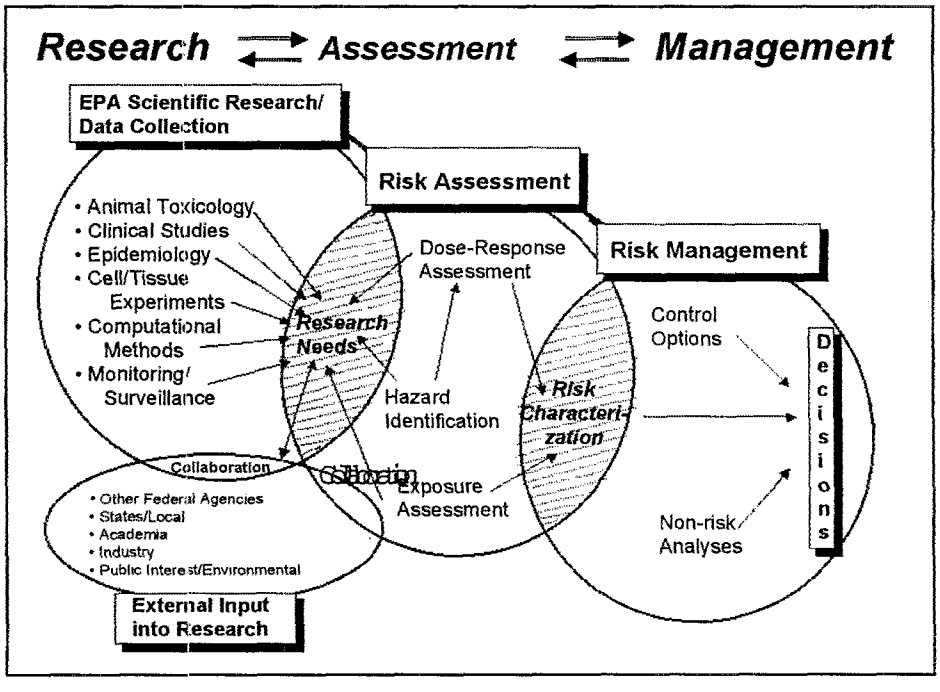
The discovery in 1997 of perchlorate-contaminated drinking water in the western United States has spurred an interagency federal task force to tackle the health implications of this finding. The belief that perchlorate could be detrimental to humans at levels found in some sources throughout the United States is driving the action, but the work is challenging. In addition to the paucity of environmental fate and toxicity information on perchlorate, there is, as yet, no proven method for removing the compound from water.



Perchlorate, a primary ingredient in solid rocket fuel, must be regularly replaced in the nation's missile and rocket inventory. It is a contaminant in groundwater and surface waters in 14 states. (Courtesy NASA)

Environmental Science and Technology / News May 1, 1998


Office of Children's Health Protection
Science Advisory Board
Administrator
Deputy Administrator
Office of Congressional and Intergovernmental Relations
Assistant Administrator
Office of Research and Development
NCEA
NERL
NHEERL
NRMRL
NCERQA
Assistant Administrator
Office of Air and Radiation
Assistant Administrator
Office of Water
Assistant Administrator
Office of Prevention, Pesticides, and Toxic Substances
Assistant Administrator
Office of Solid Waste and Emergency Response
Region 1 Boston
Region 2 New York
Region 3 Philadelphia
Region 4 Atlanta
Region 5 Chicago
Region 6 Dallas
Region 7 Kansas City, KS
Region 8 Denver
Region 9 San Francisco
Region 10 Seattle
Arizona, California, Nevada, Hawaii, American Samoa, Guam


Research
Assessment
Management
EPA Scientific Research/ Data Collection
Risk Assessment
Risk Management
• Animal Toxicology
• Clinical Studies
• Epidemiology
• Cell/Tissue Experiments
• Computational Methods
• Monitoring/ Surveillance
Research Needs
Dose-Response Assessment
Hazard Identification
Exposure Assessment
Risk Characterization
Control Options
Non-risk Analyses
Decisions
Collaboration
Collection
• Other Federal Agencies
• States/Local
• Academia
• Industry
• Public Interest/Environmental
External Input into Research

Risk Assessment is an Iterative Process

Continued Improvement

- Provisional RfD (1992, 1995) - Superfund Technical Support Center, NCEA-Cin
- Revised RfD (September 1998) - NCEA
- Refinements as required in the future

The Perchlorate Contamination Challenge

Pro-Active Partnership

- Unprecedented timeframe
- Targeted expertise

The Perchlorate Contamination Challenge Credible Science

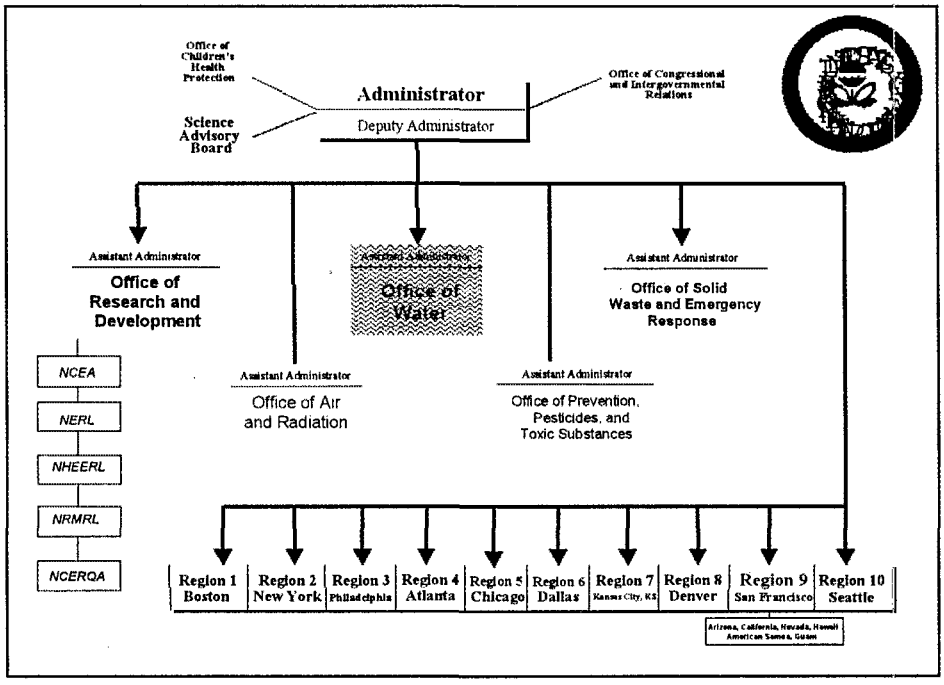
Credible Decisions

- Accurate risk characterization
- Appropriate management strategies

The Perchlorate Contamination Challenge:

An Integrated Approach

- Occurrence survey
- Stakeholder issues
- Health effects / toxicology
- Analytical methods (Detection Limit)
- Ecological impact / transport & transformation
- Treatment technology
- Technology transfer



Recent Emphasis Focuses on the Development and Use of Better Data

"The quality of risk analysis will improve as the quality of input improves. As we learn more about biology, chemistry, physics, and demography, we can make progressively better assessments of the risks involved. Risk assessment evolves continually, with re-evaluation as new models and data become available."

"Science and Judgment in Risk Assessment" (National Research Council, 1994)

Inter-Agency Perchlorate Steering Committee Stakeholder Forum

Overview and History

19-21 May, 1998

Henderson, Nevada

I P S C

I P S C

INFORMATIONAL BRIEFING

Lieutenant Colonel Dan Rogers, AFMC LO/JAV

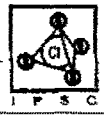
Overview

- **Purpose**
- **Historical Information and Events**
- **IPSC Composition and Focus**
- **Forum Composition and Focus**
- **Where we are and Where we are going**

Purpose of the Forum

- Gather together the leading experts currently working on the perchlorate issue
- Provide the public with real-time information on perchlorate projects
- Listen to public concerns

Inter-Agency Perchlorate Steering Committee

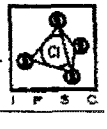


Historical Events and Chronology

(before October 1996, I couldn't spell perchlorate)

- What is Perchlorate?
- Initial Objective!
- 27 Oct 96 Cleanup and Abatement Order
- Method Detection Capability
- TERA Peer Review
- State Regulatory Partnering
- 20/21 May - Protocol Meeting and Funding
- Inter Agency Perchlorate Steering Committee

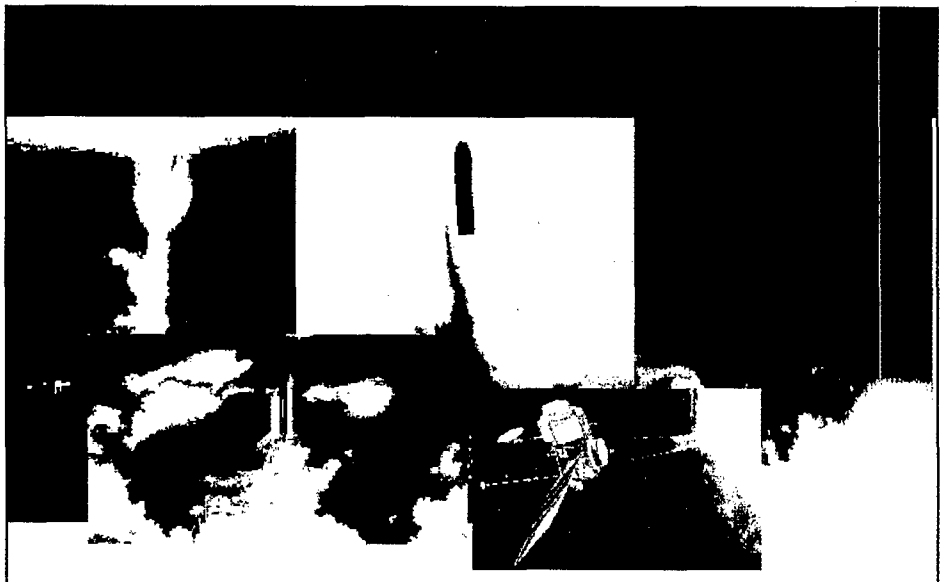
Inter-Agency Perchlorate Steering Committee



What is Perchlorate?

- **Primary Oxidizer in Solid Rockets**
  - **Titan, Minuteman, Peacekeeper, Hawk, Polaris, Space Shuttle**
  - **Army, Navy, Air Force, NASA**
- **Neither Sinker Nor Floater**
- **Very Stable in Water**

Inter-Agency Perchlorate Steering Committee



Initial Objectives

- **Evaluate and Understand Potential Health Risks Associated with Perchlorate in the Environment**
- **To Get the Best Scientific Information on the Toxicology of Perchlorate for Use by the Decision Makers and Most Importantly to the Public**
- **Partner with All Stakeholders**
  - **DoD, Industry, Research & Regulatory Community**

Inter-Agency Perchlorate Steering Committee

Integrated Approach

- **Analytical**
- **Health Effects**
- **Treatment Technology**
- **Ecological**

Inter-Agency Perchlorate Steering Committee

October 96
Central Valley Regional Water Quality Board

- Cleanup and Abatement Order
- Emphasis on Observation of Plume Movement and Detection (MDL 400 ppb)
- Time-line for Cleanup of Groundwater
- Treatment Technology
  - Aerobic Pilot Project
  - Tyndall CRADA

Inter-Agency Perchlorate Steering Committee

Analytical Method Detection Limit (or how low can you go??)

- Pre Jan 97.....400 ppb (Aerojet)
- January 97 .....100 ppb (Aerojet)
- April 97 ..... 4 ppb (DHS)
  - now replicated by CVRWQB, Aerojet and others
- Validation on both Aerojet and DHS Protocols by AF is Complete
- 1992/5 EPA "proposed" guidance level (4-18 ppb) based on provisional RfD

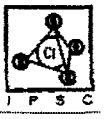
Inter-Agency Perchlorate Steering Committee

March 97 Peer Review

- Convened by TERA, Sponsored by PSG
- Overall Recommendations
  - Data insufficient
  - Solid base of studies needed
  - Minimum studies recommended
  - AF expertise recognized
- Only "known" groundwater contamination site Sacramento

Post Peer Review Activities

- Seek study funding
- Establish protocol review process
- Texpert team integration (Who?)
  - Internal (DoD)
  - External (PSG, State and Federal Researchers and Regulators)
- New source sites identified



Initial State Regulatory Partnering 21 April 97 Meeting

- Management level action officers and technical support staff
  - California DHS, DTSC, CVRWQB, OHEHA, PSG
- Partnership to serve the public
- Best value for taxpayer dollars
- Set meeting to decide best studies and protocol development

Inter-Agency Perchlorate Steering Committee

May 1997 Perchlorate Protocol Review Meeting

- 20/21 May 1997 - Cincinnati
- Expert
  - USAF (AL/HSC/BCA), PSG, DHS, DTSC, OEHHA, EPA Superfund Office, NCEA, Ohio State, U of Cincinnati, Cytec Industries
- Goal?
  - Prioritized List of Reasonable Studies
  - Information Exchange
- California Still the Only "Site"

Inter-Agency Perchlorate Steering Committee

Results

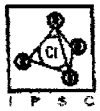
- Prioritized list of studies
- Promise to assist in protocol development
- Focus on the goal without regard to cost
- Share final protocol information with the public
- Begin studies as soon as possible
- Partnering to secure needed funding

Inter-Agency Perchlorate Steering Committee

Inter Agency Perchlorate Steering Committee (13 Jan 98)

- Purpose
- Sub Committees to address critical areas
- Membership
  - Federal and State Governmental Agencies
  - Tribal Representatives
- Meetings Open to Public
- Coordinate with AWWA-RF
- Public Stakeholder Forum

Inter-Agency Perchlorate Steering Committee



Inter-Agency Perchlorate Steering Committee
-as of 21 May 1998-

Executive Committee
Peter Grevatt (EPA-OSWER)
Kevin Mayer (EPA-IX)
Lt Col Dan Rogers (DoD-USAF)
Annie Jarabek (EPA-NCEA)
Mike Osinski (EPA-OW)

Ecological Impacts (T/T)
Mark Sprenger (EPA-OERR)
Cornell Long (DoD-USAF)

Analytical
Captain Dave Tsui (DoD-USAF)
Steve Pia (EPA-NERL)
Howard Okamoto (Cal-DHS)
Sanwat Chaudhuri (Utah DEQ)

Health Effects/Toxicity
Dave Mattie (DoD-USAF)
Annie Jarabek (EPA-NCEA)

Peer Review
Peter Grevatt (EPA-OSWER)

Treatment Technology
Ed Urbansky (EPA-NRMRL)
Wayne Praskins (EPA-IX)
Jim Hurley (DoD-USAF)

Forum Composition and Focus

- **Bring together the experts in health effects/toxicology, ecological impacts/transport and transformation, analytical methods and treatment technology**
- **Occurrence information**
- **Provide information on current initiatives**
- **Hear public and stakeholder concerns**

Inter-Agency Perchlorate Steering Committee

Where We Are Today?

- Funded toxicology initiatives underway
- Funded treatment initiatives underway
  - AWWA-RF
  - Air Force, Army, NASA
- Partnership initiatives strong
  - Liaison with States of California, Nevada and Utah, Tribal Representation
  - Expect EPA revised RfD end Sept 98 with an external peer review in Oct 98

Inter-Agency Perchlorate Steering Committee

Is There a Bottom Line?

- Goal - best scientific information to ensure protection of the nation's drinking water supply
- To get the best scientific information on the toxicology and occurrence of perchlorate to the decision makers and most importantly to the public
- Maintain an integrated approach
- Develop methods and technology as required

Inter-Agency Perchlorate Steering Committee

Bottom Line (continued)

- **There are no limits to the success of this innovative project because of its talented and dedicated team (They don't really care who gets the credit!)**

Inter-Agency Perchlorate Steering Committee I P S C

Lt Col Dan Rogers

AFMC LO/JAV
Environmental Law Directorate
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937-257-7287
937-257-0537 (fax)
drogers@jag.af.mil

Inter-Agency Perchlorate Steering Committee I P S C

PERCHLORATE OCCURRENCE

Kevin Mayer
Superfund Program
U.S. EPA, Region 9

PERCHLORATE OCCURRENCE

- History - Before 1997
- Perchlorate Users
  - Facilities
  - Locations
- Perchlorate in the Environment
  - Occurrence Nationwide
  - California Wells
  - Nevada

HISTORY - Before 1997

- 1980s - Aware of Perchlorate in CA, NV
- 1985-86 - San Gabriel Valley
- 1990s - Rancho Cordova (ppm)
- 1992-95 - Provisional Reference Dose (ppb range)
- 1997 - Analytical breakthrough

San Gabriel Valley Superfund Site

- Large, complex groundwater site
- Perchlorate suspected
- Colorimetric test (0.02-0.05 mg/l) in 1985
- Preliminary data positive
- Toxicological request in Dec. 1985

San Gabriel Valley Superfund Site

- Quality Assurance Problems
  - Sample blanks - False positives
  - Cannot Validate Data
- All Perchlorate Results Rejected
- ATSDR: Better Analysis First
- No Immediate Developments in Analysis

Agency for Toxic Substances and Disease Registry - ATSDR (January 21, 1986):

"...Given the proprietary nature of the laboratory method for quantification and the poor quality assurance results noted, the **data do not prove that perchlorate ion has actually been found.** If the presence of perchlorate ion is confirmed, the **scientific database** on this ion is **insufficient to generate either an acute or longer-term health advisory for drinking water**"

"... The minimal acute toxicity data available suggest that one or two ppm perchlorate ion would not represent an immediately acute and substantial threat to the public health. The ATSDR does not consider this level to be "safe" in the absence of experimental data.."

Aerojet General Superfund Site (Rancho Cordova)

- Perchlorate > 1 mg/l in groundwater
  - Detectable by EPA method (Ion Chromatography)
- Region 9 requests Provisional RfD from NCEA EPA Nat'l Center for Environmental Assessment
- December, 1992: 4 micrograms/liter (ppb)
- October, 1995 range: 4-18 ppb
- Analytical Limit 400 ppb

USES of PERCHLORATE

- 90% Solid Rocket Fuel Oxidizer
- Explosives
- Fireworks and Pyrotechnics

PERCHLORATE SHIPMENTS

- Manufacturer's Information
- About 150 facilities
- 35+ States
- Most Information in Last 20 Years

PERCHLORATE in the ENVIRONMENT

- UTAH wells, TEXAS surface water
- American Water Service Survey
  - 425 wells, 7 hits (4 states)
- CALIFORNIA
  - Over 500 Water Supply Wells Tested
  - About 110 Reported, More than 30 Wells over 18 ppb

PERCHLORATE in the ENVIRONMENT

- UTAH wells, TEXAS surface water
- American Water Service Survey
  - 425 wells, 7 hits (4 states)
- CALIFORNIA
  - Over 500 Water Supply Wells Tested
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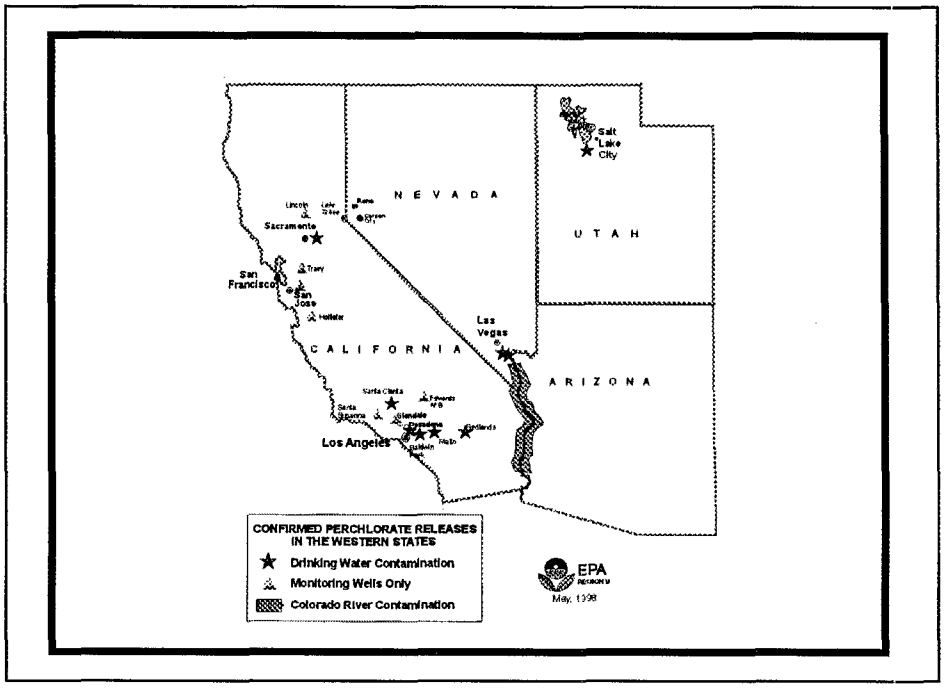
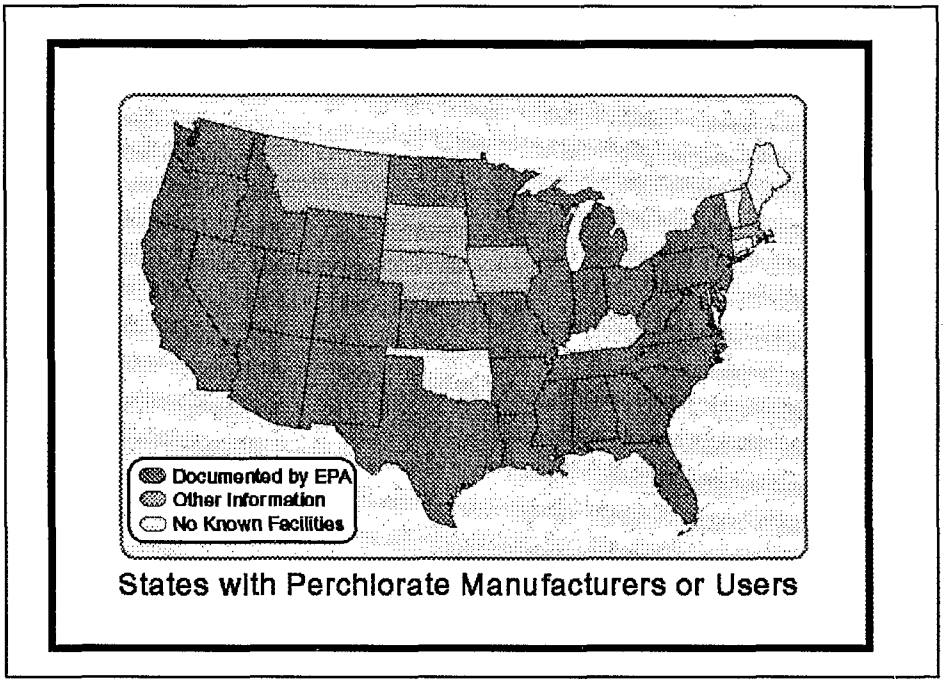
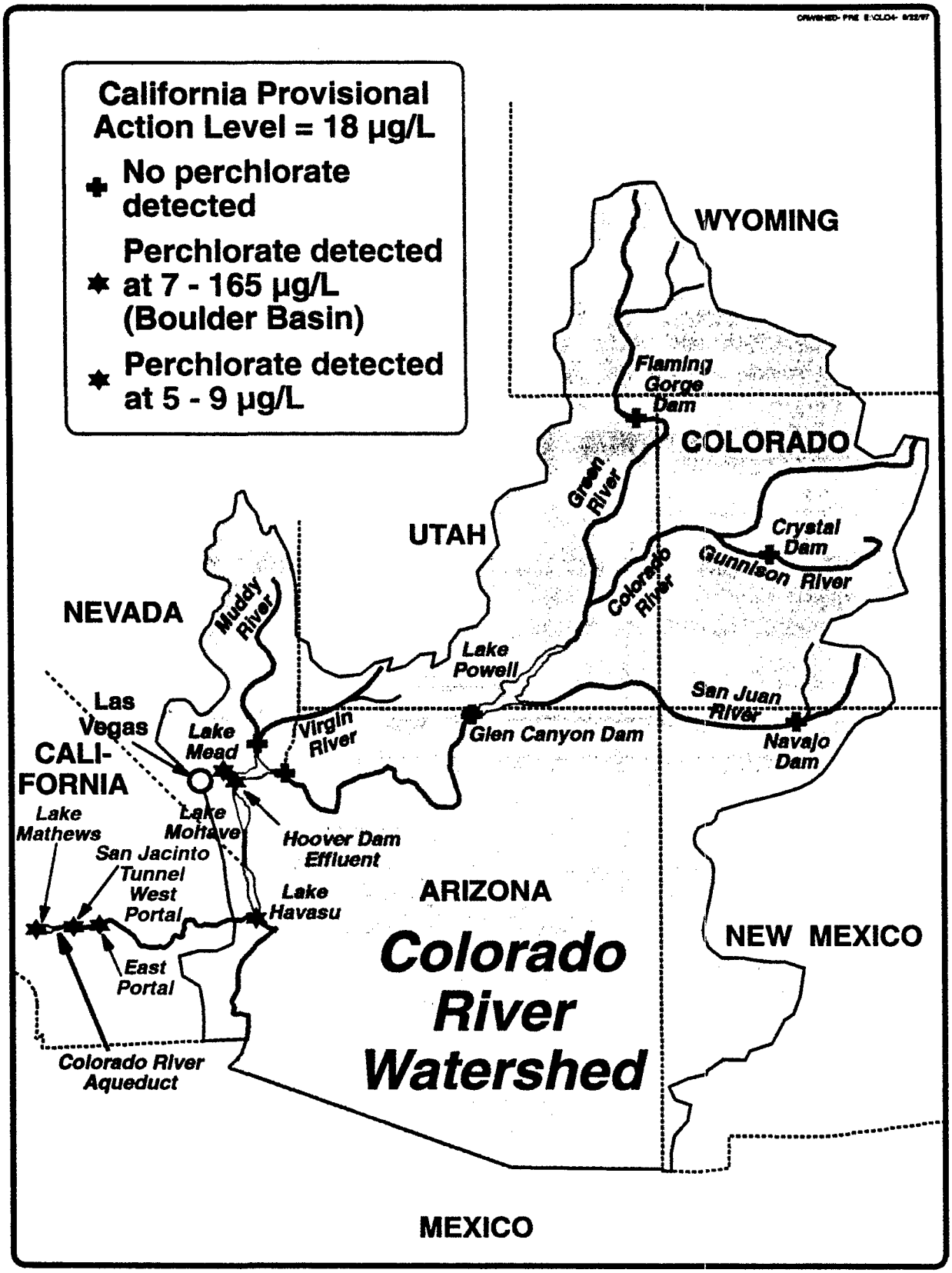
COLORADO RIVER and LAKE MEAD

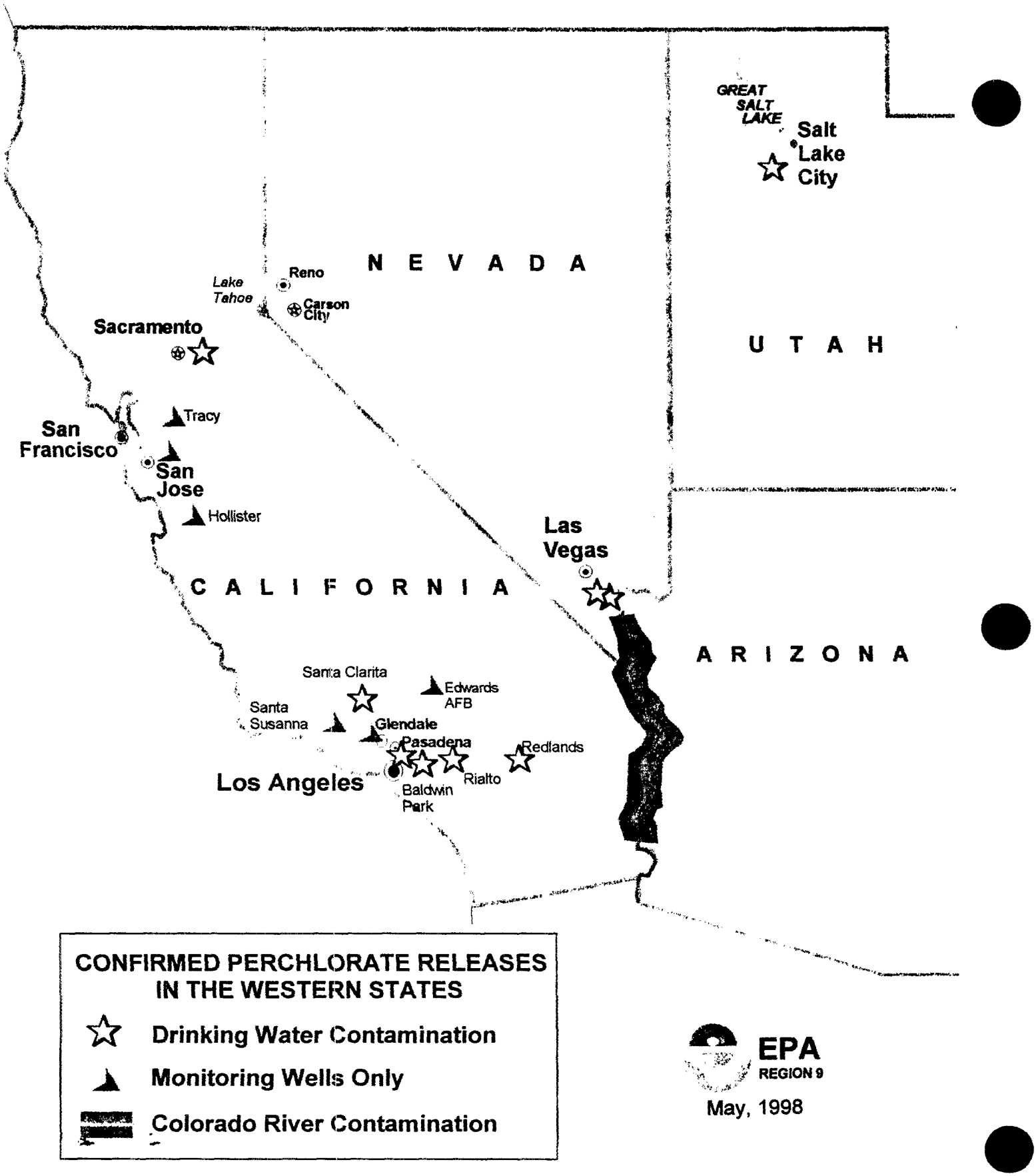
- Southern California Aqueduct
- Lake Havasu (Colorado River)
- Lake Mead
- Non-Detect Upstream


Salt Lake City
NEVADA
UTAH
Sacramento
San Francisco
San Jose
Las Vegas
CALIFORNIA
ARIZONA
Los Angeles
CONFIRMED PERCHLORATE RELEASES IN THE WESTERN STATES
Drinking Water Contamination
Monitoring Wells Only
Colorado River Contamination
EPA
May, 1998


Documented by EPA
Other Information
No Known Facilities
States with Perchlorate Manufacturers or Users



Perchlorate Detection in the Colorado River Watershed

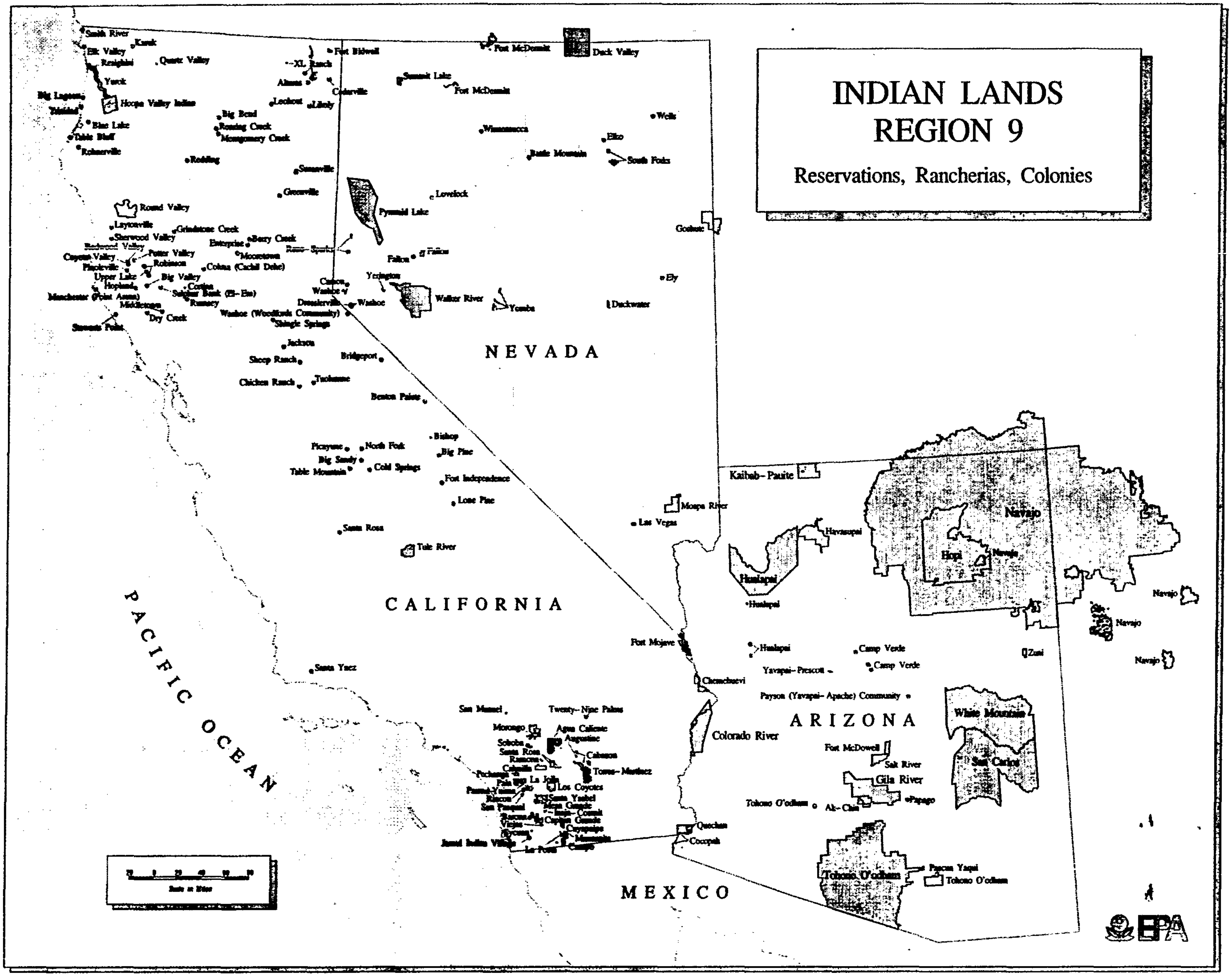


CONFIRMED PERCHLORATE RELEASES IN THE WESTERN STATES

- ☆ Drinking Water Contamination
- ▲ Monitoring Wells Only
- ▬ Colorado River Contamination

EPA
REGION 9

May, 1998

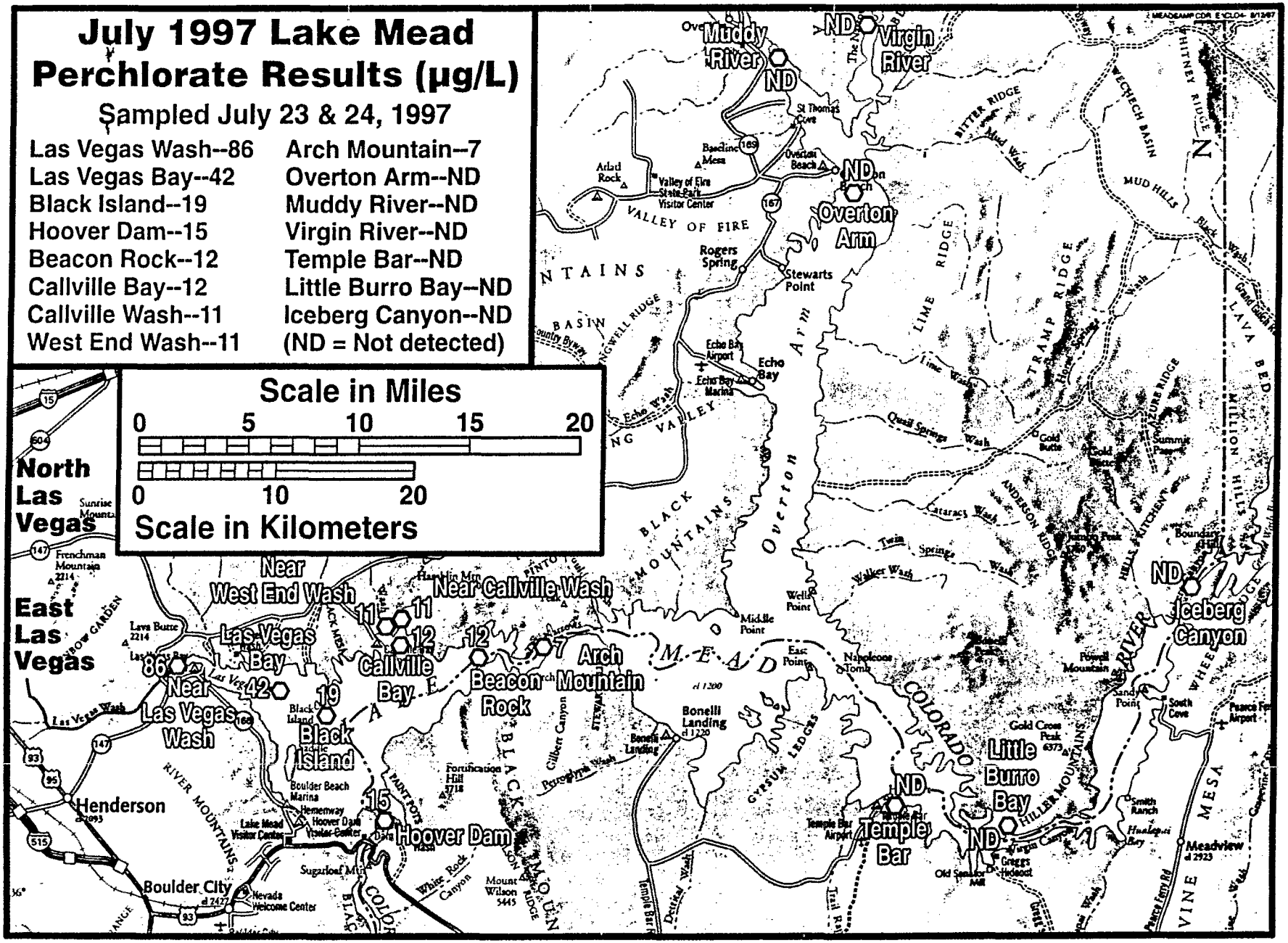

INDIAN LANDS
REGION 9
Reservations, Rancherias, Colonies
NEVADA
CALIFORNIA
ARIZONA
PACIFIC OCEAN
MEXICO
Smith River
Hoopa Valley Indian
Round Valley
Pyramid Lake
Walker River
Duck Valley
Fort McDermitt
Summit Lake
Fort Bidwell
Winnemucca
Battle Mountain
Elko
South Fork
Wells
Goshute
Lovelock
Fallon
Yerington
Yomba
Duckwater
Ely
Bishop
Big Pine
Fort Independence
Lone Pine
Tule River
Santa Rosa
Santa Ynez
Las Vegas
Moapa River
Kaibab-Paiute
Havasupai
Hualapai
Navajo
Hopi
Zuni
Fort Mojave
Chemehuevi
Colorado River
Camp Verde
Yavapai-Prescott
Payson (Yavapai-Apache) Community
White Mountain
San Carlos
Fort McDowell
Salt River
Gila River
Ak-Chin
Papago
Tohono O'odham
Pascua Yaqui
Quechan
Cocopah
San Manuel
Twenty-Nine Palms
Morongo
Agua Caliente
Augustine
Cabazon
Torres-Martinez
Soboba
Santa Rosa
Ramona
Cahuilla
Pechanga
La Jolla
Los Coyotes
Santa Ysabel
Rincon
San Pasqual
Mesa Grande
Capitan Grande
Viejas
Sycuan
Cuyapaipe
Manzanita
Campo
La Posta
Jamul Indian Village
EPA


DRAFT
INDIAN LANDS
CALIFORNIA
Indian Lands
City/Town
County Line
The Indian Reservations, Rancherias and Colonies represented on this map were compiled from coverages provided by the U.S. Bureau of Indian Affairs (US BIA), U.S. Bureau of Reclamation (USBR) and tribal agencies. Boundaries were also taken from 1990 TIGER Line files where better data was unavailable. For each reservation, the largest scale and most up to date data available was used.
Reservation labels on this map represent the names most commonly used by the residents of the reservations. These names were compiled in consultation with the U.S. EPA Indian Program Office.
If corrections are required, contact Cheryl Healey at (415) 744-1754.
US EPA Region 9, GIS Center
Toth C. Anteon Corporation
May, 1998
EPA
Redding
Sacramento
Stockton
San Francisco
Oakland
San Jose
Santa Cruz
Modesto
Fresno
Bakersfield
Santa Barbara
Los Angeles
San Bernardino
San Diego

July 1997 Lake Mead Perchlorate Results (µg/L)

Sampled July 23 & 24, 1997

Las Vegas Wash--86	Arch Mountain--7
Las Vegas Bay--42	Overton Arm--ND
Black Island--19	Muddy River--ND
Hoover Dam--15	Virgin River--ND
Beacon Rock--12	Temple Bar--ND
Callville Bay--12	Little Burro Bay--ND
Callville Wash--11	Iceberg Canyon--ND
West End Wash--11	(ND = Not detected)



PERCHLORATE INVESTIGATION

LAS VEGAS VALLEY/LAKE MEAD

Nevada is one of seven Colorado River Basin states that relies in some part on the Colorado River for its drinking water. The river forms the southeastern border of the state and flows south from the Las Vegas area forming the border between California and Arizona and on into Mexico.

This slide shows the LV valley with the hydrographic basin outlined in yellow. The valley is surrounded on all sides by mountain ranges; the Las Vegas Range to the north, the Spring Mountains to the west, the McCulloughs to the south and the Muddy Mountains to the east. The central area is the City of Las Vegas, Henderson is located in the southeastern portion of the valley. All water in the Las Vegas Basin flows towards the southeastern portion of the valley and drains out of the valley through Las Vegas Wash to Lake Mead. Groundwater in the Henderson area flows north towards the wash. This shallow groundwater is naturally very high in total dissolved solids and is not used as a drinking water source. About 85% of the valley's drinking water comes from Lake Mead which is extracted at Saddle Island, about 6 miles downstream of where the wash flows into Lake Mead. The remaining 15% of drinking water is from groundwater extracted from the Las Vegas Valley Water District's municipal well field and from additional wells located in the northwest part of the valley. The water that flows through Las Vegas Wash makes up approximately 1.5% of the water in Lake Mead. The majority, 97%, of the water in the lake is from the Colorado River with some small contribution from the Muddy and Virgin Rivers.

In the late summer of 1997, NDEP was made aware by officials of the Metropolitan Water

District of Southern California of the presence of perchlorate in the Colorado River in the low part per billion range. Samples taken below Hoover Dam indicated the presence of perchlorate at 8 ppb. Sampling conducted in Lake Mead by Metropolitan in July 1997 showed no perchlorate in all of the tributaries to the lake except Las Vegas Wash. A high of 86 ppb was detected at Northshore Road near Las Vegas Wash just above Las Vegas Bay which decreased in concentration the farther they moved towards the east.

Follow-up sampling was conducted by Metropolitan in August and found a perchlorate concentration of 680 ppb at Northshore Rd., which decreased to 14 ppb as you moved away from the wash towards Hoover Dam. Sampling in Lake Mead was also conducted by the Southern Nevada Water Authority which confirmed Metropolitan's findings.

At this point NDEP began the first of a three phase investigation designed to identify source areas and regional groundwater impacts in the Henderson area. Initial activities involved sampling 9 locations in or near Las Vegas Wash.

One wash sample was taken above all three treatment plants, one was taken below each of the three plant outfalls, samples were taken at the Pabco Road crossing, just west of Lake Las Vegas, and one at Northshore Road. One sample was taken in Duck Creek, a tributary to Las Vegas Wash and a sample was taken of the discharge from the Pittman Bypass Outfall which drains non-contact cooling water from the BMI industrial facility where Kerr McGee is located.

The results of this sampling indicated the presence of relatively low concentrations of perchlorate in the low ppb range in the western reach of LV Wash which increased suddenly to the 500 ppb range at Pabco Road. Higher concentrations of approximately 1 ppm were found west of Lake Las Vegas and at Northshore Road. The Duck Creek sample also showed a relatively low concentration of 14 ppb perchlorate similar to the western reach of the wash.

When this data collection was complete, a sampling program was initiated by NDEP in order to obtain shallow groundwater data in the Henderson/Pittman area. Due to the fact that both Kerr McGee and Pepcon produced ammonium perchlorate in the Henderson area, NDEP also requested these two companies begin collecting data from existing wells, or in the case of the former Pepcon facility, from newly installed wells. The results of this sampling concluded that perchlorate was present in the groundwater beneath both Kerr McGee and the former Pepcon facility and had migrated off-site of both locations.

Both companies were then asked to accept responsibility for completing Phases II and III of the investigation. Phase II of the investigation involved the compilation of existing groundwater and lithologic information in order to identify data gaps. When the data gaps were identified, additional field investigation was planned in order to define the groundwater flow paths to the wash. Additionally, the companies were requested to immediately begin research into viable remediation technologies. This phase of the investigation was expected to take approximately 6 months.

Phase III was to involve the actual implementation of a system designed to intercept contaminated groundwater before it reached Las Vegas Wash. The Division feels that extraction and treatment of groundwater is more feasible than treatment of the wash due to the high flow volumes which are on the order of 125 million gallons per day through the wash.

Results of Kerr McGee's investigation have indicated that significant groundwater flow is primarily through high permeability zones within the paleochannels in the unconsolidated gravels and streambed deposits in this area. The flow is generally in a south to north direction with ultimate discharge in the wash. Research conducted by EPA about 15 years ago in this area which is referred to as the Pittman Lateral, discovered a large channel which is believed to be

carrying the vast majority of perchlorate contaminated water from the Kerr McGee facility to the wash. Perchlorate concentrations of water sampled from this channel were found to be on the order of 500 ppm.

Kerr McGee has been drilling numerous borings in thearea east of the City of Henderson wastewater treatment plant in order to identify the flow path that this paleochannel takes to the wash. It appears that the paleochannel flows from the site, through the Pittman Lateral and under the City of Henderson's wastewater treatment plant. They are currently investigating the area to the north of the treatment plant in order to find the channel as close to the wash as possible. The objective of this work is to locate the most appropriate location for groundwater interception and extraction for ultimate treatment or disposal before it discharges in the wash. A report with their findings is expected by mid-June.

Additionally, Kerr McGee is in the process of building an 11-acre evaporation pond on their plant site. The pond will take perchlorate contaminated water extracted from the plant site and will serve as a source control mechanism. Completion of the pond is expected by late summer.

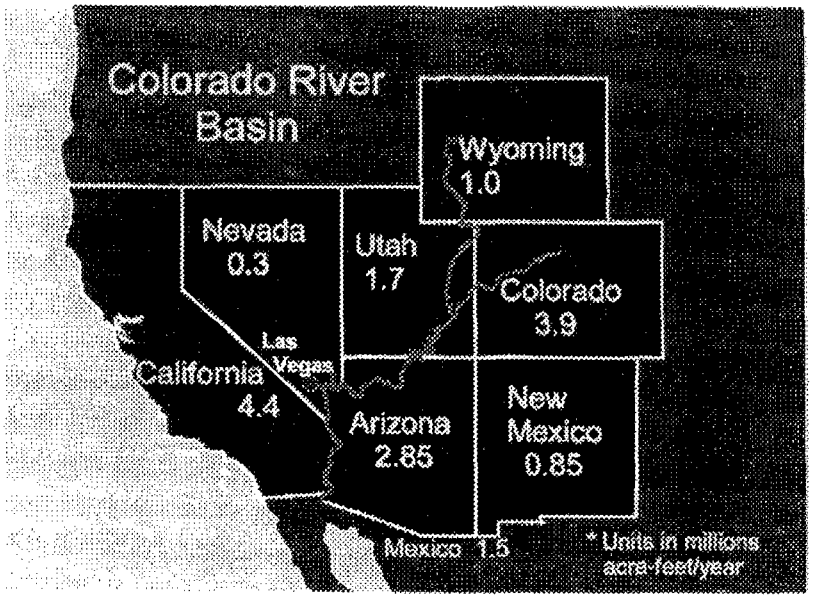
Pepcon's investigation involved the installation of 42 groundwater monitoring wells and sampling of 45 existing wells in order to delineate the extent of their plume and determine its impact to Las Vegas Wash. Based on their sampling results, it has been concluded by American Pacific Corporation that the plume which originated from the former Pepcon site does not comingle with the plume from Kerr McGee's facility. Additionally, they have concluded that their plume does not impact Las Vegas Wash in a significant manner.

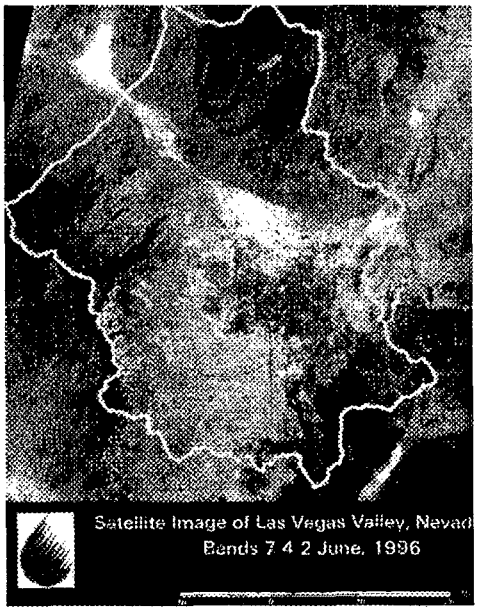
American Pacific has recommended quarterly monitoring of select groundwater wells near their plume and that a remedial options analysis be performed. At this point, NDEP has not had a

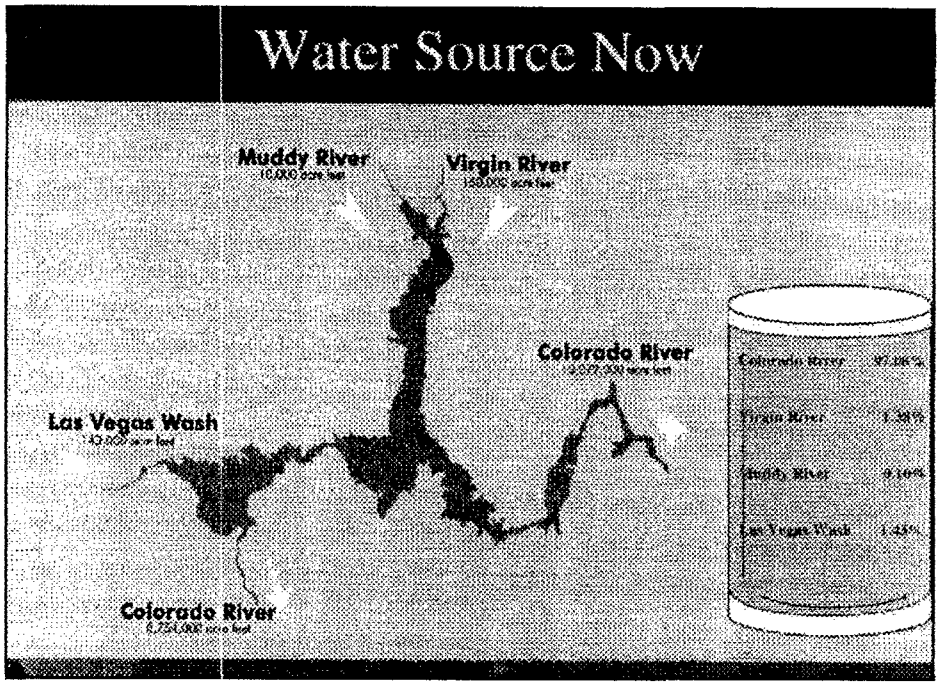
chance to review this report and cannot state whether we will concur with these conclusions and recommendations.

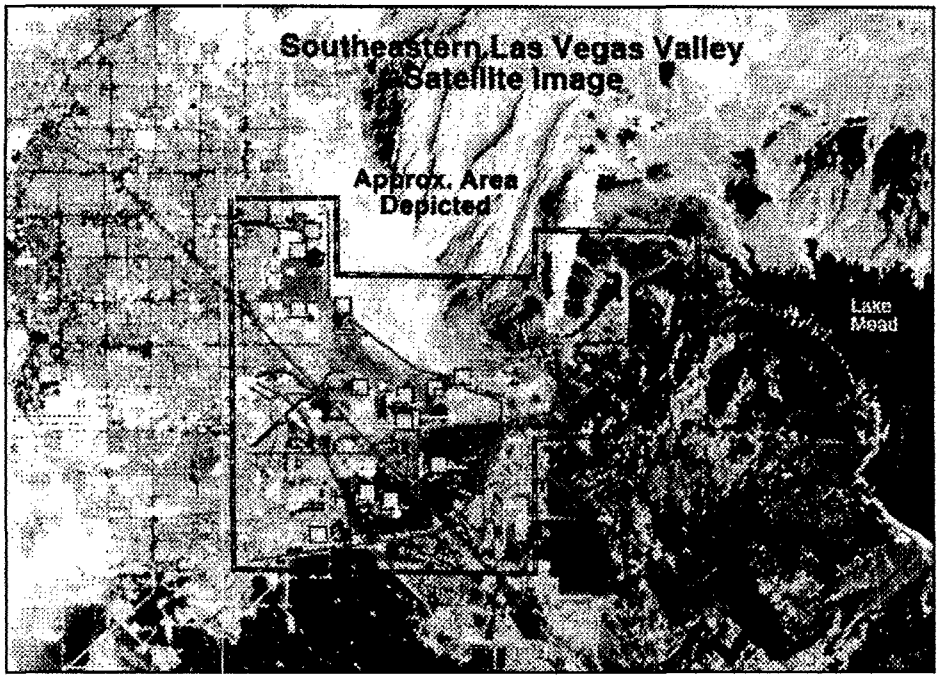
Because Phase 2 of the perchlorate investigation was expected to take 6 months, both SNWA and NDEP wanted to maintain a database that would allow us to determine whether perchlorate concentrations in Las Vegas Wash or Lake Mead were changing significantly. Las Vegas Wash sampling has continued since August, initially on a weekly basis, and later on a bimonthly basis, at Northshore Road. Perchlorate results at this location have stayed relatively constant. They fluctuate on a weekly basis but always stay within a range between 550 and 1000 ppb.

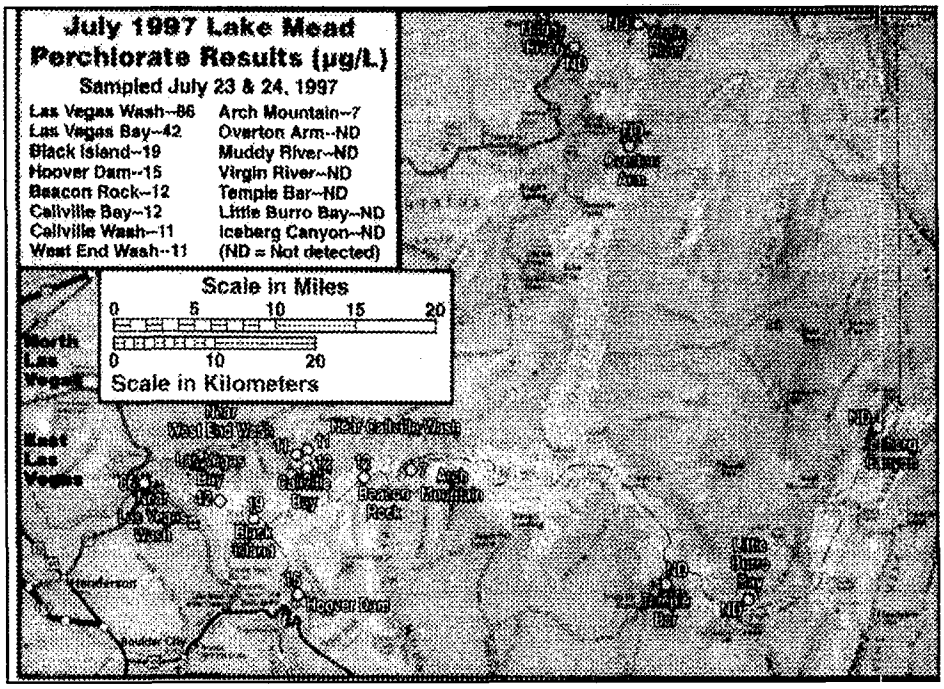
SNWA conducts monthly sampling of raw Lake Mead water at the drinking water intake and of finished water before it enters their distribution system. Initial sampling indicated low ppb perchlorate levels last summer, which increased to 16 ppb in December when the lake destratified due to colder weather conditions. The perchlorate concentrations have since decreased somewhat and are expected to continue decreasing during the summer's warm weather.

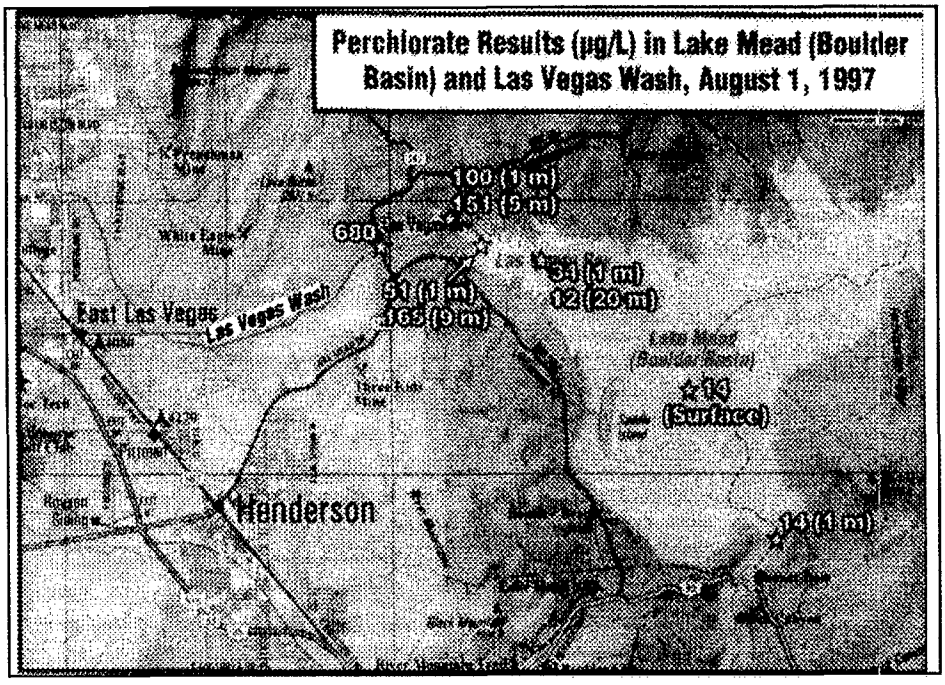

Colorado River Basin
Wyoming 1.0
Nevada 0.3
Utah 1.7
Colorado 3.9
Las Vegas
California 4.4
Arizona 2.85
New Mexico 0.85
Mexico 1.5
* Units in millions acra-feet/year

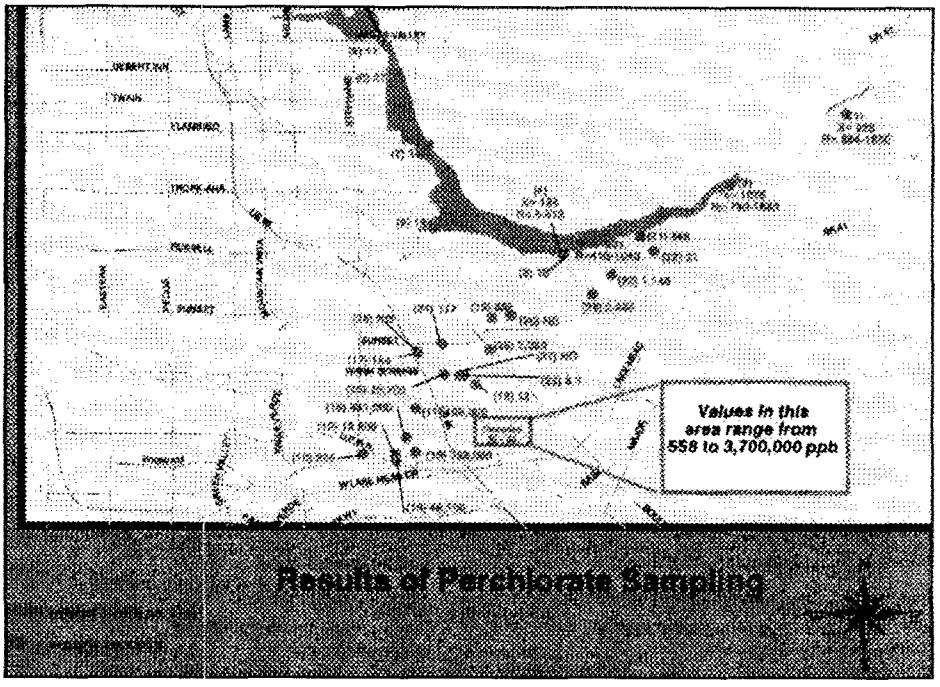

Satellite Image of Las Vegas Valley, Nevad
Bands 7 4 2 June, 1996


Water Source Now
Muddy River
Virgin River
Colorado River
Las Vegas Wash
Colorado River


Southeastern Las Vegas Valley
Satellite Image
Approx. Area
Depicted
Lake
Mead


July 1997 Lake Mead
Perchlorate Results (µg/L)
Sampled July 23 & 24, 1997
Las Vegas Wash--86
Las Vegas Bay--42
Black Island--19
Hoover Dam--15
Beacon Rock--12
Callville Bay--12
Callville Wash--11
West End Wash--11
Arch Mountain--7
Overton Arm--ND
Muddy River--ND
Virgin River--ND
Temple Bar--ND
Little Burro Bay--ND
Iceberg Canyon--ND
(ND = Not detected)
Scale in Miles
0 5 10 15 20
0 10 20
Scale in Kilometers
North Las Vegas
East Las Vegas
Las Vegas Wash
Henderson


Perchlorate Results (µg/L) in Lake Mead (Boulder Basin) and Las Vegas Wash, August 1, 1997
100 (1 mi)
151 (5 mi)
680
61 (6 mi)
165 (9 mi)
64 (1 mi)
12 (20 mi)
(Surface)
East Las Vegas
Las Vegas Wash
Henderson
14 (1 mi)



THREE PHASE INVESTIGATION

Phase I

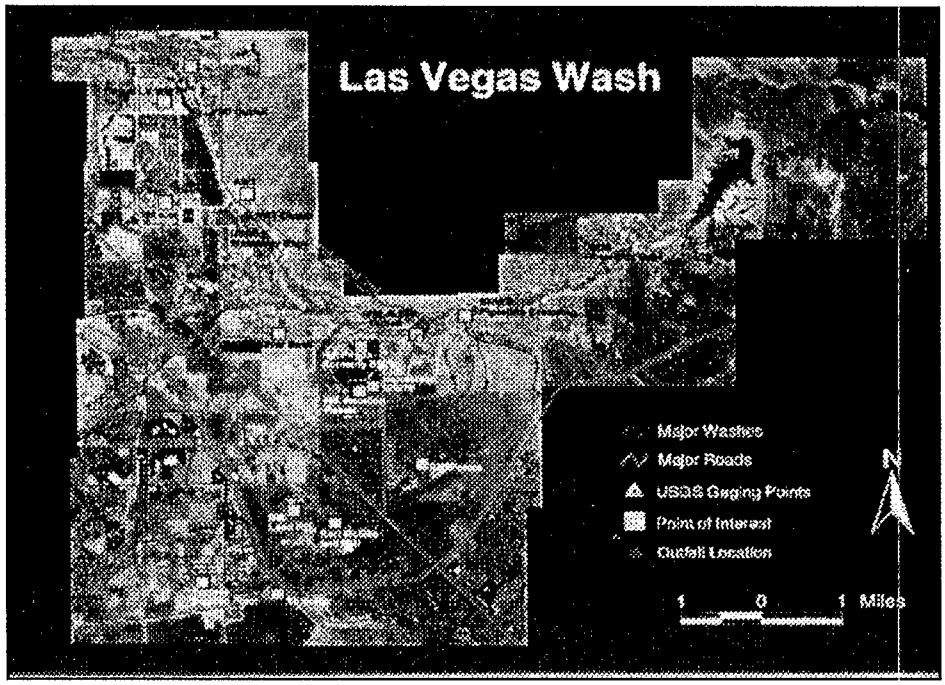
- source area identification
- regional groundwater impacts

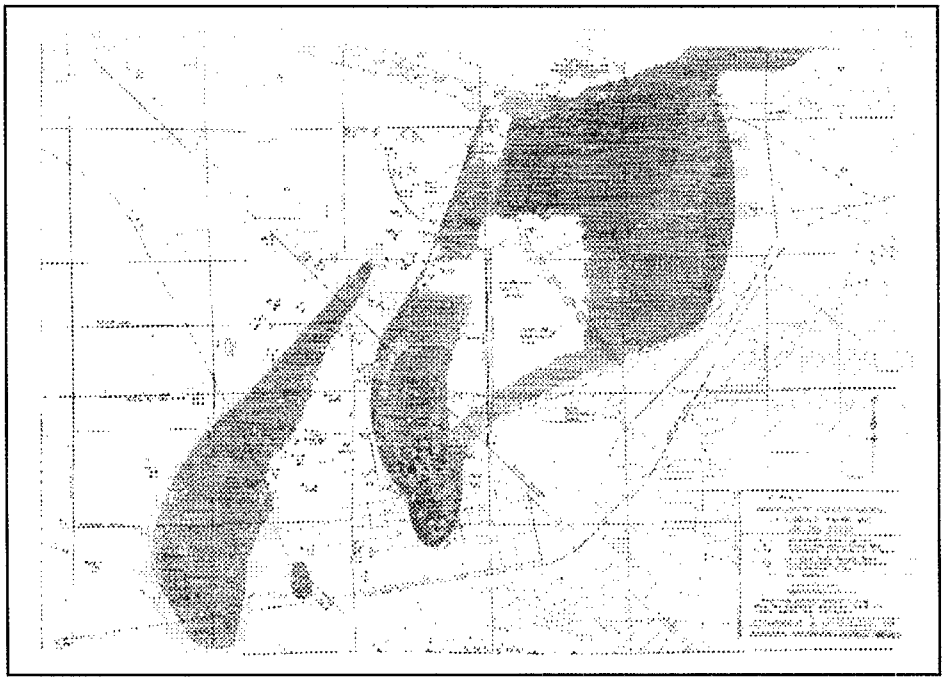
Phase II

- compile existing groundwater and lithologic information
- identify data gaps
- complete hydrogeologic investigation defining groundwater flow paths to wash
- research viable remedial technologies

Phase III

- design and implement remediation system designed to intercept groundwater before reaching Las Vegas Wash


Las Vegas Wash
Major Washes
Major Roads
USGS Gaging Points
Point of Interest
Outfall Location
N
1 0 1 Miles



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 9
75 Hawthorne Street
San Francisco, CA 94105-3901

May 6, 1998

MEMORANDUM

SUBJECT: Teleconference on Perchlorate with Tribal Environmental Representative

FROM: Kevin P. Mayer, H-6-4

TO: Perchlorate Steering Committee
Tribal Participants
Keith Takata, Director, Region 9 Superfund Division

On April 24th, we held a teleconference with Matt Leivas (Chemehuevi), Connor Byestewa (CRIT), John Swenson (Cocopah), Dr. Karen Medville (ASU, Intertribal Science Advisor) and myself to discuss perchlorate issues critical to Native American Tribes.

Communication was the principle concern expressed:

1) EPA and the California web site give the impression that perchlorate contamination of water supplies is an extensive, serious problem. There is no indication that tribes in California other than those along the Colorado River have been made aware of the issue by either federal or state officials.

2) It is apparent that state and local agencies and water suppliers were identified as important stakeholders very early in the process while tribes were not initially considered.

3) Even after the tribes were contacted, the level of involvement has not been adequate. A primary example is the scheduling conflict between the Stakeholder Forum in Henderson and the National Tribal Environmental Council meeting on the exact same dates. The tribal representatives strongly recommended another stakeholders meeting at a later date to allow full participation by the tribes.

4) Input from tribes was not solicited for the report to congress on perchlorate issues (due April 27) nor for the perchlorate conference background papers. EPA should provide these documents to the tribes as soon as they are released and be prepared to incorporate tribal issues in subsequent documents.

5) There is no evidence of participation by Bureau of Indian Affairs, the Indian Health Service or the Bureau of Reclamation.

6) The tribes requested a list of names, phone numbers and addresses of the participants in the Interagency Perchlorate Steering Committee

Attendance at Henderson

Key environmental people from several of the tribes along the Colorado River will be unable to attend the Henderson Stakeholders Forum. Many tribes have only one senior environmental official who would be able to fully participate and contribute on technical aspects of perchlorate effects on tribal resources. In addition to providing meeting proceedings, there should be a follow-up meeting for tribes to allow interchange with the range of agencies and scientific disciplines present at the stakeholders forum.

Resources for sampling and interpretation of technical results are needed by the tribes. The Chemehuevi spent tribal resources to test their water supplies for perchlorate and confirmed the presence of perchlorate at about 7 ppb in Lake Havasu. None of the other tribes have had their water tested for perchlorate. The non-detect results from Yuma need to be confirmed.

Other Priorities

The tribes recognize that EPA and the other agencies place a high importance on researching the toxicity of perchlorate in human drinking water and on developing treatment technologies. However, after these two priorities there appears to be a sharp drop-off in commitment to study some issues important to the tribes. Among the information needs are:

Analysis of perchlorate uptake and translocation into irrigated crops

Research on a range of agricultural effects (e.g., productivity, accumulation in soil)

Effects on fish and wildlife.

Other potential and perceived effects on recreational use of the river. Recreation impacts (on fishing, swimming, boating) are a very high concern not only for protection of tribal members but for the important recreational and resort business.

Position statements

Some discussion was held concerning the most effective way of communicating the needs of the various tribes. There is no single spokesperson for the tribes since they are different entities with different concerns that do not always overlap. At least one tribe is planning to write a letter stating that tribe's position. This letter will be available to be presented at the Henderson Stakeholder's Forum, and I committed to reading it to the attendees. Letters to elected officials and to Carol Browner were also mentioned for prioritizing resources to perchlorate issues.

Chemehuevi Indian Tribe

P.O. Box 1976 Havasu Lake, CA 92363 • (760) 858-4219 Fax: (760) 858-5400

May 12, 1998

United States Environmental Protection Agency, Region 9
Mr. Kevin P. Meyer, H-6-4, Perchlorate Steering Committee
75 Hawthorne Street
San Francisco, California 94105-3901

Dear Mr. Meyer,

In behalf of the Chemehuevi Indian Tribe I hereby submit our written comments to the Perchlorate Steering Committee.

The Chemehuevi Tribe was never formally notified by any governmental agency (Federal, State or Counties), about the discovery of Perchlorate in the Colorado River. An article in a newspaper was our source of notification.

Due to many unknown facts about Perchlorate, the Tribal Water Department "Tribal Utility" was directed to take water samples from our two domestic wells, as well as two samples from the Colorado River at North Catfish Bay and at the irrigation pumping station in the bay itself.

The test results determined that the two domestic wells showed no contamination. The two test samples taken from the river were sent to an EPA certified laboratory for analysis and confirmed the results at 6.8 ppb of Perchlorate.

In 1997, the Chemehuevi Tribe passed an Ordinance regarding the discharge of any contaminants into any river, steam or waterway within the exterior boundary of the reservation. This ordinance in effect protects the tribe's water resources and allows the tribe to challenge the responsible parties.

Our irrigation pump is situated in Catfish Bay and we presently have 100 acres under cultivation, with a remainder of 1800 acres yet to be developed. The tribe is environmentally conscious and has decided to make our farming operation totally organic. This raises a question regarding potential contamination to the crops as well as the soil through irrigation from the Colorado River.

The most immediate concern we have is the potential hazards to individuals who come in contact with contaminated water. We understand that the EPA currently

does not have a safe limit standard, but the State of California's Environmental Protection Agency does. They established a safe minimum standard of 18 ppb for an adult, 150 pounds and over. However, this raises questions regarding the harmful affects on persons under 150 pounds, such as children.

The tribe is also very much concerned about the entire eco-system from where the contamination enters the river and the affects it has on fish & wildlife. The Tribe established a Conservation Department, which has the authority and responsibility to oversee all Natural Resources on the reservation. The Chief Conservation Officer has concerns about the perchlorate contamination and the possible affects on soil along the shoreline and on fish & wildlife. The biological effects on the latter are of utmost concern because of human consumption.

The Chemehuevi Tribe owns an enterprise called "Havasu Landing Resort & Casino", which is located on the western shore of Havasu Lake. Our primary attraction is outdoor recreation, namely the Colorado River and the lake itself. Each year thousands of visitors come to the reservation to enjoy this precious resource, to either fish, hunt, swim, water ski and/or to enjoy boating. The Perchlorate contamination would more than likely keep people away, thus causing irrefutable harm to the success of our business.

We would like to be kept abreast of any future meetings regarding Perchlorate and would like to be active members of the Steering Committee, since we do have *decreed, perfected water rights*. We appreciate your cooperation thus far and look forward to seeing you in Henderson, Nevada next week.

If you have any questions or need any further clarification you may call me directly or contact Ms. Sandy Hillary or Mr. Matthew Leivas, Sr. at the Tribe's Environmental Department.

Sincerely,

Edward D. Smith

Mr. Edward D. Smith
Vice Chairman

cc. Chem. Tribal Council,
Environmental Department
BIA, Parker, AZ. & Phx. Area Office
IHS
ITCA
L.J.M., Attorney
USDA, NRCS, Mr. Rick Aguayo

RESOLUTION CT-98-18

COCOPAH TRIBAL COUNCIL

A Resolution to Express Concern and Indignity the Tribe Suffers From the Announced Release of the Perchlorate Chemical Into The Colorado River. Be it resolved by the Tribal Council of the Cocopah Indian Tribe, in general meeting assembled on May 8, 1998

WHEREAS, the Cocopah Indian Tribe is a nation of people with pride and dignity who reside along the Colorado River; and

WHEREAS, the Cocopah Indian Tribe has a long and continuous history of cultural relationship with the Colorado River; and

WHEREAS, the Cocopah Indian Tribe relies upon the Colorado River for its waters; and

WHEREAS, any activities of peoples or institutions that can effect the Colorado River upstream of the Cocopah Nation may or does have impact upon the Cocopah people; and

WHEREAS, the continued quality of the Colorado River is of direct concern of the Cocopah Indian Nation; and

NOW, THEREFORE, BE IT RESOLVED by Tribal Council of the Cocopah Indian Tribe that any activities regarding the release of any form of perchlorate into the Colorado River is considered a serious offense against the Cocopah people and must be brought to the attention of the Cocopah Tribal Council and its scientific staff; and

BE IT FINALLY RESOLVED that the Tribal Council Chairperson and Tribal Secretary, or their designated representatives, are authorized to sign any and all documents necessary to implement this action.

The foregoing resolution was on May 8th duly approved by a vote of 4 for. 0 against and 0 abstaining. by the Tribal Council of the Cocopah Indian Tribe. pursuant to authority in the Constitution and By Laws of the Tribe. This resolution is effective as of the date of its adoption.

COCOPAH INDIAN TRIBAL COUNCIL
By

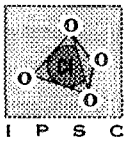
Chairperson

Secretary

Background and Objectives of Ongoing Studies

Annie M. Jarabek
National Center for Environmental Assessment
U.S. Environmental Protection Agency

Perchlorate Stakeholders Forum
Sponsored by the IPSC
Henderson, NV
19-21 May 1998



Outline

- Background
  - Definition of the RfD
  - Derivation of the RfD
  - Basis of the provisional RfD
- Review of perchlorate database
- Recommended new studies
  - Description of different study designs
  - Objectives of each study
  - Strategy for synthesis of data
- Summary

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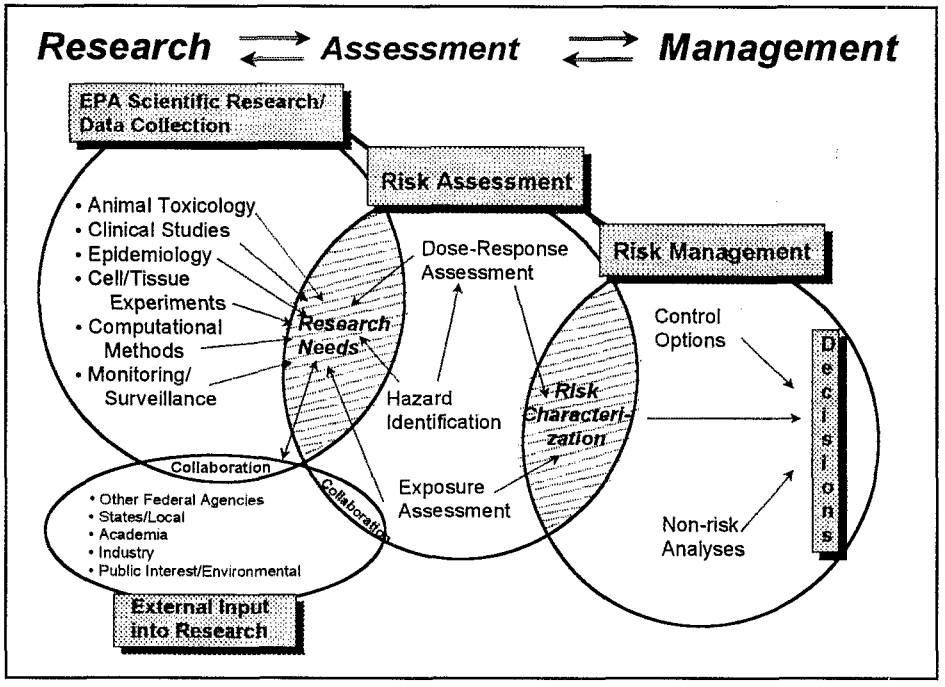
Definition

An oral reference dose (RfD) is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious noncancer health effects during a lifetime.

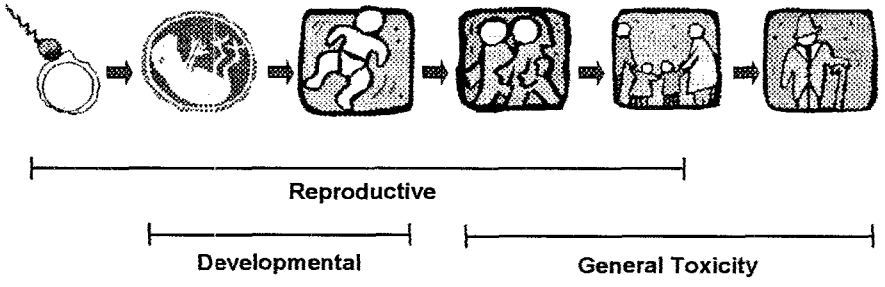


Minimum Data Base for Derivation of an RfD

Mammalian Data Base**	Confidence	Comments
A. Two Chronic Oral Bioassays in Different Species B. One 2-Generation Reproductive Study C. Two Developmental Toxicity Studies in Different Species	High*	Minimum Data Base for High Confidence
One Subchronic Oral Bioassay	Low	Minimum Data Base for Estimation of an RfD

* Rationale is to address all potentially critical life stages
** Rationale is to use different species to evaluate variability in species sensitivity unless a particular laboratory animal model is more appropriate

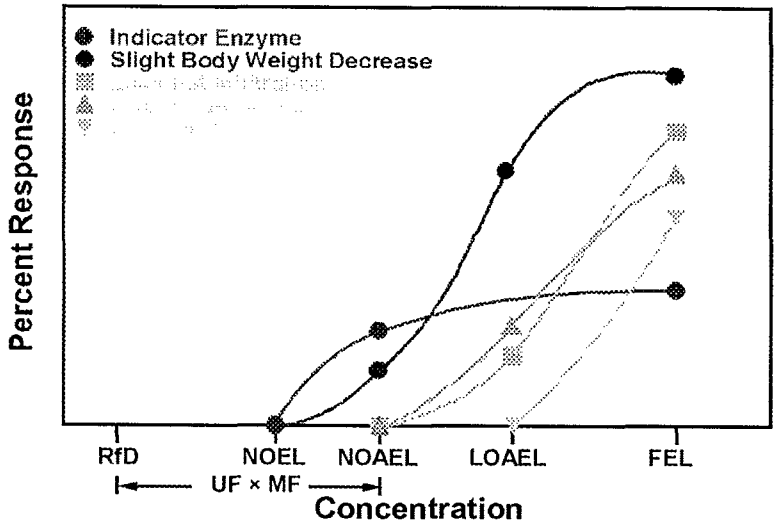
A High Confidence RfD is Based on Data that Addresses All Potentially Critical Life Stages.



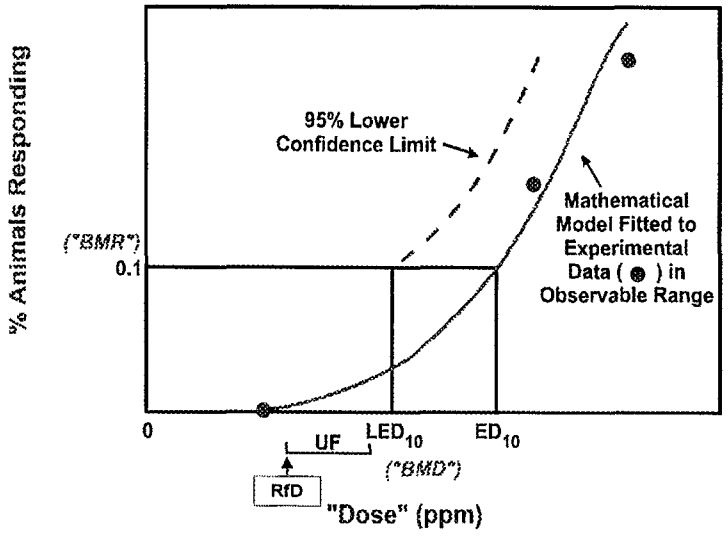
RfD Derivation

- Hazard identification and data array analysis
- Designation of effect levels (NOAEL, BMD)
- Choice of critical effect
- Dosimetric adjustment
- Application of uncertainty factors (UF)
- Characterization of uncertainty (confidence levels)

Data Array and Oral Reference Dose (RfD) Derivation



"Benchmark Dose" Approach to Dose-Response Analysis for Noncancer Endpoints



$$RfC = \frac{NOAEL^*[HED]}{UF \times MF}$$

Where:

NOAEL*[HED] =

The NOAEL or equivalent effect level obtained with an alternate approach (*), dosimetrically-adjusted to a human equivalent dose [HED].

UF =

Uncertainty factor(s) applied to account for the extrapolation required from the characteristics of the experimental regimen to the assumed human scenario, and

MF =

Modifying factor to account for scientific uncertainties in the study(ies) chosen as the basis for the operational derivation, e.g., poor statistical power or exposure characterization.

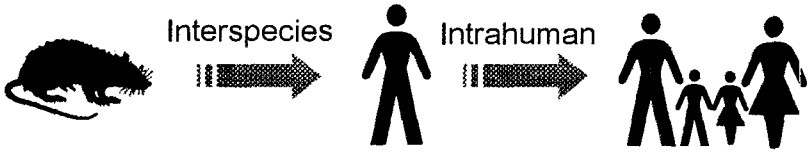
Factors for Uncertainties in Applied Extrapolations

- 10_H Human to Sensitive Human
- 10_A Experimental Animal to Human
- 10_S Subchronic to Chronic Duration
- 10_L LOAEL(HEC) to NOAEL(HEC)
- 10_D Incomplete to Complete Data Base

Modifying Factor

MF Professional Assessment of Scientific Uncertainties of the Study and Data Base not Explicitly Addressed Above. Default for the MF is 1.0 e.g., applied for small sample size or poor exposure characterization.

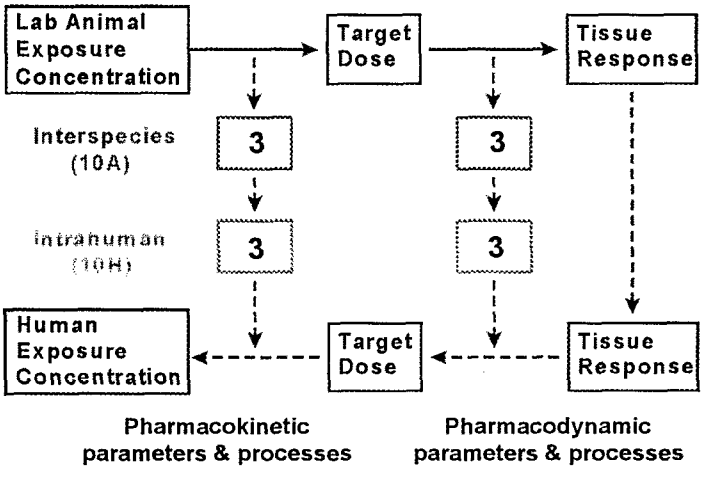
Extrapolation Uncertainties



Rat to Human

Variability Across Humans

Schematic of UF Components Incorporated Into Exposure-Dose-Response Characterization



Basis of the Provisional RfD

- **Initial correspondence to EPA Region IX (Dec 92) from Superfund Health Risk Technical Support Center (NCEA-Cin)**
- **Principal study = Stanbury & Wyngaarden (1952)**
- **NOAEL = 0.14 mg/kg-day for 100% iodide release**
- **UF = 1000**
  - intrahuman variability (10)
  - less than chronic data (10)
  - database deficiencies (10)
- **Drinking water criteria = 3.5 ppb based on 70 kg / 2 L water**

Second Provisional RfD (1995)

- **Revision based on PSG submission to Superfund Health Risk Technical Support Center (NCEA-Cin)**
- **Same principal study and NOAEL**
- **Different UF**
  - intrahuman variability (10)
  - less than chronic data (10)
  - database deficiencies decreased (3)
- **Drinking water criteria = 18 ppb based on 70 kg / 2 L water**

Provisional RfD March 1997 External Peer Review

- **Proposed by TERA**
- **Same prinicipal study, critical effect**
- **Another, different UF = 100**
  - intrahuman reduced (3)
  - subchronic to chronic (3)
  - LOAEL to NOAEL (3)
  - Database deficiencies (3)

March 1997 External Peer Review Process

- Independent experts selected from government, industry, academia, consulting firms and environmental groups by TERA Board of Trustees
- Conflict of interest disclosed and discussed
- Review lasted 3 hours and included:
  - presentation by sponsor
  - discussion by review panel of database, hazard identification, dose-response derivation, and other issues
  - opportunity for registered observers to comment
  - polling panel for consensus
  - identification of outstanding issues

March 1997 External Peer Reviewers

- Dr. Robert Benson, U.S. EPA, Region VIII
- Dr. John Christopher*, California EPA
- Dr. Gary Diamond, Syracuse Research Corporation
- Dr. Marvin Friedman, Cytec Industries, Inc.
- Ms. Annie Jarabek, U.S. EPA, National Center for Environmental Assessment
- Ms. Bette Meek, Health Canada
- Dr. Kenneth Poirier, Procter and Gamble Company
- Dr. Jon Reid, University of Cincinnati
- Ms. Ruthann Rudel, Silent Spring Institute
- Experts Available to Peer Review Panel
  - Dr.James Fagin, University of Cincinnati Department of Endocrinology
  - Dr. Charles Capen, Ohio State University Department of Veterinary Biosciences
  - Dr. Daniel Caldwell, principal investigator of the Caldwell et al. (1996) study

* Dr. Christopher was not polled for consensus

March 1997 External Peer Review

- Inadequate data base for derivation
- Available mechanistic insights suggest special studies and synthesis strategy
- Eight (8) additional new categories of studies recommended

Deficiencies of Clinical Data

- Adult subjects
- Typically subjects with thyroids altered by disease or other treatments
- Few pregnant subjects
- Acute or short-term exposure duration
- Limited range of doses

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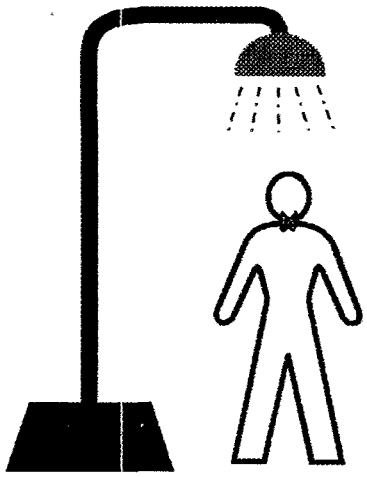
Established Perchlorate Toxicity



The only systematically studied and established effect is the anti-thyroid effect due to competitive inhibition of iodine uptake.

Susceptibility

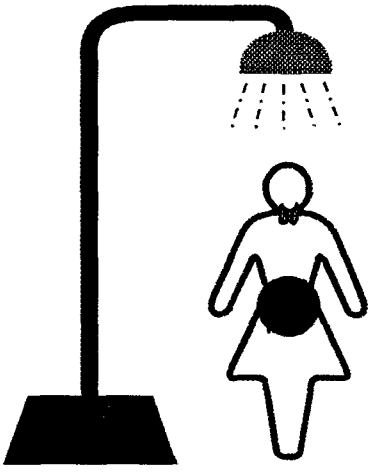
The potential for increased susceptibility is due to factors that influence:

(1) Exposure e.g., activity patterns and location

(2) Deposition / uptake and the internal target tissue dose (i.e., pharmacokinetic parameters) and toxicant-target interactions, e.g., metabolism rates or pathways

(3) Tissue sensitivity (pharmacodynamics) - conditions which alter or enhance target tissue response, e.g., age, nutritional status, or disease states

Potential Perchlorate Toxicity



Anti-thyroid effect in pregnant women might cause adverse effect in developing fetus.

Additional Suggested Target Tissues

- Reproductive function
- Immune function
  - aplastic anemia
  - leukopenia

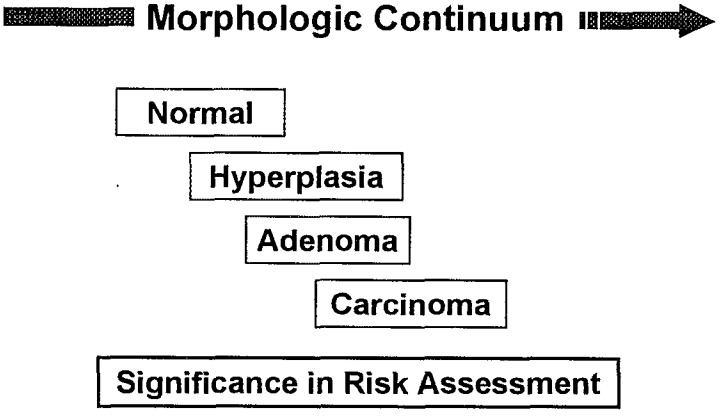
Mechanisms of Anti-Thyroid Mediated Neoplasia in Rodents

- DNA Directed:
  - X - rays
  - 131 I
  - Genotoxic chemicals
- Indirect
  - Partial thyroidectomy
  - Transplantation of TSH-secreting pituitary tumors
  - Iodide deficiency
  - Chemicals inhibiting iodide uptake
  - Chemicals inhibiting thyroid peroxidase
  - Chemicals inhibiting TH
  - Chemicals inhibiting conversion of T3 & T4
  - Chemical inhibiting hepatic thyroid hormone metabolism and excretion

Mode of Action Provides Important Insight to Characterization of Toxicity

- A chemical's influence on the molecular, cellular, and physiological functions in producing tumors
- Prolonged depression of TH causes a feedback that leads to upregulation of TSH which leads to thyroid gland hyperplasia
- Genotoxic?

Proliferative Lesions Thyroid Follicular Cells in Rodents



Existing Data Summary

- Target tissue appears to be the thyroid but available testing not comprehensive across endpoints
- Anti-thyroid effects would differ among adult versus developing fetus, children
- Anti-thyroid effects associated with benign neoplasia development in rats; a nonlinear process
- Genotoxicity not characterized
- Relevancy to human risk of rat tumors not established; presumed protective

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- Summary

Recommended Studies

- 90-Day subchronic bioassay
- Developmental neurotoxicity study
- Genotoxicity assays
- Mechanistic studies
- ADME - Absorption, Distribution, Metabolism and Elimination
- Developmental study
- 2-Generation reproductive toxicity study
- Immunotoxicity

90-Day Subchronic Bioassay

- Tests for additional target tissues
- Minimum database for RfD derivation
- Added additional tests for:
  - reproductive parameters
  - mutagenic effects in bone marrow
  - thyroid hormone levels
  - recovery
- Objective is to ascertain if anti-thyroid effect is critical and its dose-response

Developmental Neurotoxicity Study in Rats

- Examines potentially critical effect and population: evaluates nervous system (structure and function) of fetal, newborn, and young animals
- Added thyroid histopathology and thyroid hormone level determinations to characterize anti-thyroid effect in offspring

Genotoxicity Assays

- Tests for toxicity to DNA
- Provides mode-of-action information to evaluate potential for carcinogenicity
- May impact consideration of uncertainty factor for less than chronic data

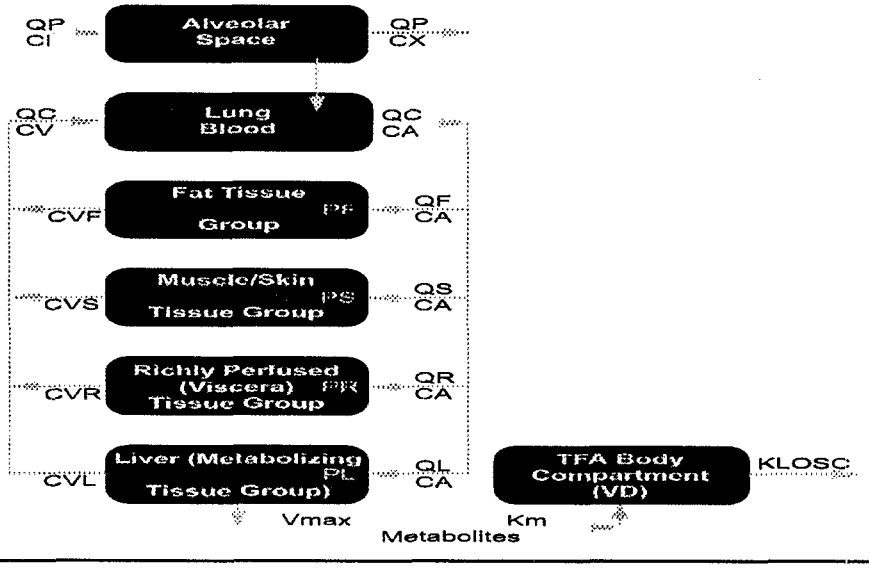
Mechanistic Studies

- Aid to quantitative interspecies extrapolation - basis to extend PBPK model
- Additional developmental studies to evaluate thyroid TH in fetal and post-natal periods
- Determine relative sensitivity of fetal/postnatal thyroid versus adult
- Determine relative sensitivity of rat versus human

ADME study

- Literature review of perchlorate discharge test
- Protocols proposed to evaluate perchlorate kinetics, iodine inhibition kinetics and thyroid hormone homeostasis
- Basis for development of physiologically-based pharmacokinetic (PBPK) model

PBPK Model Schematic



Developmental Study in Rabbits

- Endpoint required for greater confidence in database, may reduce UF for data deficiencies if not critical effect
- Definitive test for toxicity during organ development (birth defects)
- Added additional groups, hormone analysis and thyroid histopathology to evaluate second species

2-Generation Reproductive Toxicity Study

- Evaluates fertility of adults and viability of (toxicity in) offspring in rats
- Tests for reproductive parameters over two generations
- Added analysis of thyroid hormones and thyroid histopathology at various time points
- Endpoint required for greater confidence in database, may reduce UF for database deficiencies if not critical effect

Immunotoxicity Study

- Evaluates immune system structure and function
- Motivated by case reports of aplastic anemia and leukopenia
- May reduce UF for database deficiencies if not critical effect

Recommended Studies Summary

Study	Description	Use in assessment
1. Developmental neurotoxicity + TH	Evaluates nervous system in fetal and postnatal rats	Potentially critical effect; comparison of developmental versus adult effects on TH
2. 90-Day subchronic bioassay + TH + repro + genotox + recovery	Tests for other target tissues; evaluates effect on TH in young adult rats	Minimum database for RfD dose-response for TH in young adult rats; additional info on other; may allow decrease in UF for database deficiencies
3. Genotoxicity assays	Tests for toxicity to DNA	Mode of action information for thyroid neoplasia; may reduce UF for database deficiencies
4. Mechanistic studies	Evaluate mechanism of TH response and sensitivity in rats and humans	Interspecies extrapolation; determine susceptible subpopulation

Recommended Studies Summary

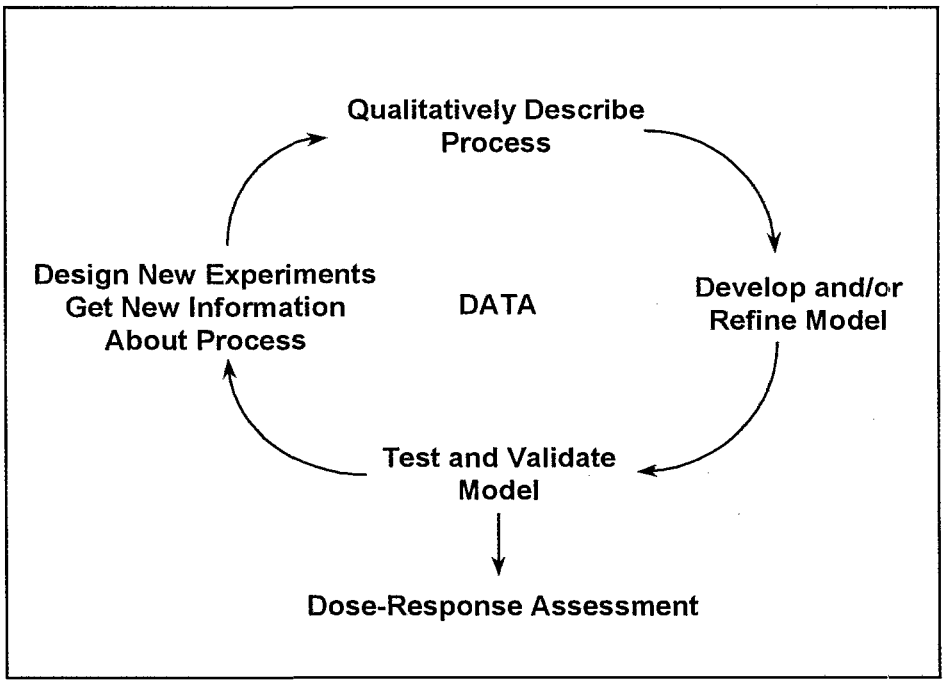
Study	Description	Use in assessment
5. ADME studies	Characterizes absorption, distribution, metabolism and elimination in rats and humans; iodine inhibition and perchlorate kinetices, hormone homeostasis	Interspecies extrapolation
6. Developmental study + TH	Evaluates birth defects in rabbits	Potentially critical effect; data in second species for TH effects; may reduce UF for database deficiencies
7. 2 - Generation reproductive toxicity + TH	Evaluates fertility of adult rats and toxicity in offspring over two generations	Potentially critical effect; may reduce UF for database deficiencies
8. Immunotoxicity	Evaluates immune system structure and function	May reduced UF for database deficiencies if not critical effect

Outline

- Background
  - Definition of the RfD
  - Derivation of the RfD
  - Basis of the provisional RfD
- Review of perchlorate database
- Recommended new studies
  - Description of different study designs
  - Objectives of each study
  - Strategy for synthesis of data
- Summary

Revised RfD

- Data across comprehensive array of endpoints to establish target tissue
- Mechanistically-motivated special studies to characterize critical dose-response relationships
- Future refinements as required by new data



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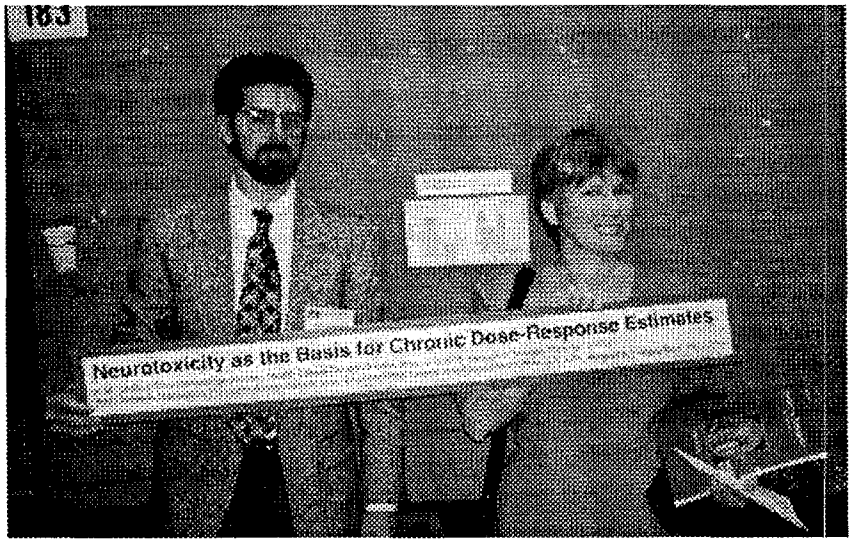
Mechanisms of Thyroid Toxicity

Kevin M. Crofton
Neurotoxicology Division
National Health and Environmental Effects Laboratory
US Environmental Protection Agency
Research Triangle Park NC

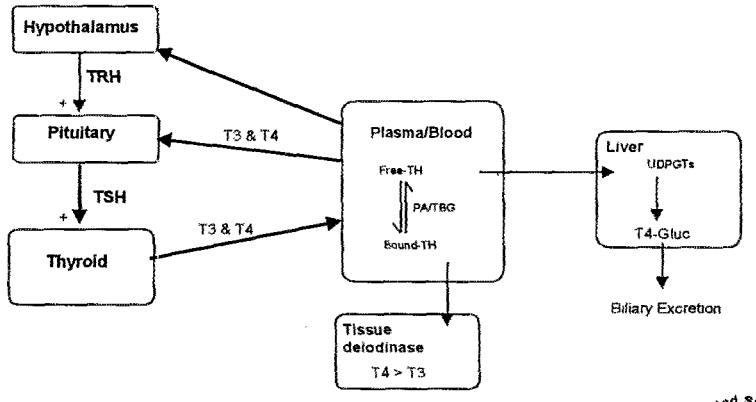


Outline

1. Introduction to thyroid hormones
2. Effects of perchlorate
3. Effects of the disruption of thyroid hormones
   - Thyroid hyperplasia and neoplasia
   - Developmental abnormalities
4. Uncertainties

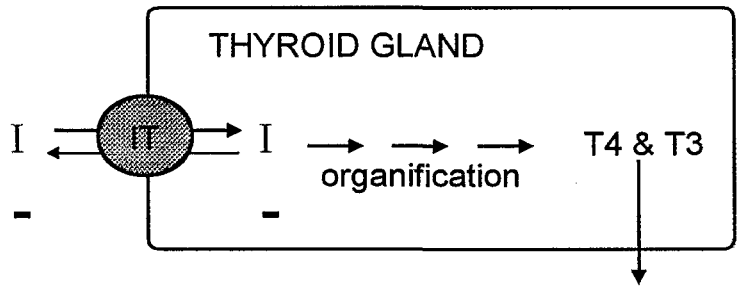
National Health and Environmental Effects Laboratory

Hypothalamus-Pituitary-Thyroid-Liver Axis



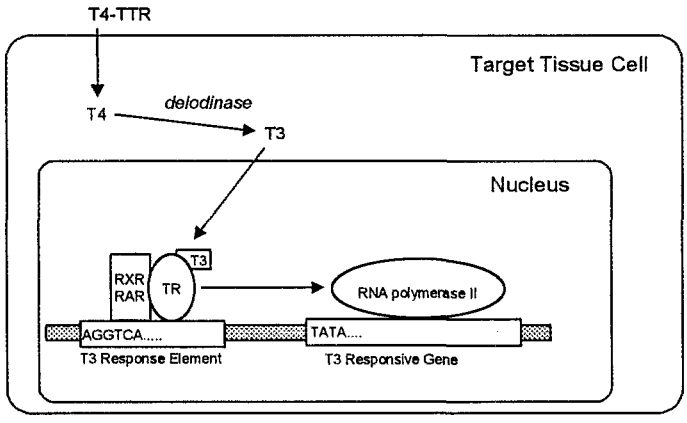
National Health and Environmental Effects Laboratory

Iodine and the Thyroid Gland



National Health and Environmental Effects Laboratory

Thyroid Hormone Receptors and Thyroid Response Elements



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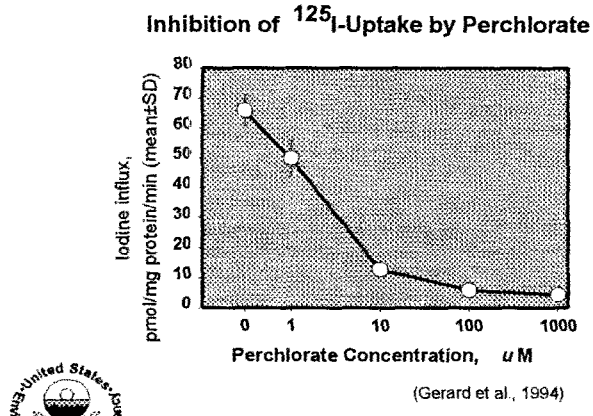
Targets for Environmental Chemicals

- Thyroid Gland
  - ➡uptake process
  - ➡organification
  - ➡release
- Plasma Transport Proteins
- Tissue Deiodinases
- Hepatic Glucuronidation and Sulfation

National Health and Environmental Effects Laboratory

In Vitro Thyrotoxicity of Perchlorate



(Gerard et al., 1994)

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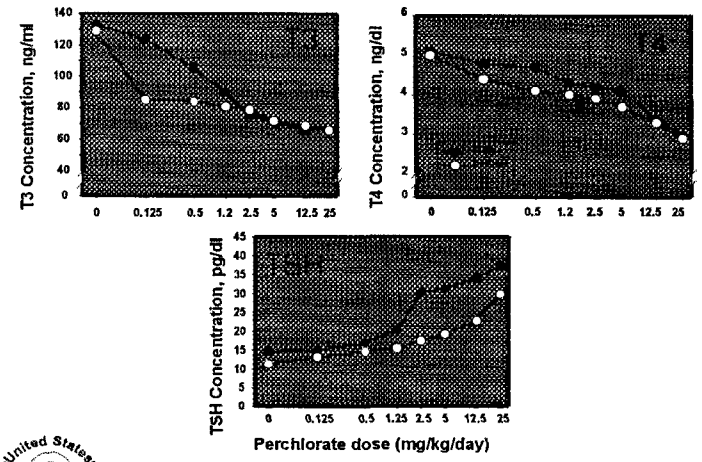
14-Day In Vivo Perchlorate Study



(Caldwell et al., 1994)

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Effect of TH disruption

- **Adult**
  - **Main effect of prolonged depression of TH is upregulation of TSH which leads to thyroid gland hyperplasia**
- **Developmental**
  - **Main effect is the disruption of developmental processes**

National Health and Environmental Effects Laboratory

Main Symptoms/Effects of Hypothyrodism

Developmental

- delayed reflex ontogeny
- impaired fine motor skills
- deaf-mutism, spasticity
- gait disturbances
- mental retardation
- speech impairments

transient disruption leads to permanent effects

Adult

- run down, slow, depressed,
- sluggish, cold, tired
- dryness and brittleness of hair
- dry and itchy skin, constipation
- muscle cramps
- increased menstrual flow

transient disruption leads to transient effects

*thyroid tumors in rodents

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Data Deficiencies

- **Long-term periodic exposures**
  - **Perchlorate kinetics**
  - **Thyroid hormone homeostasis**
- **Effects during development**

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Uncertainties in Risk

1. Animal to Human Extrapolation
2. Age-Dependent Sensitivity

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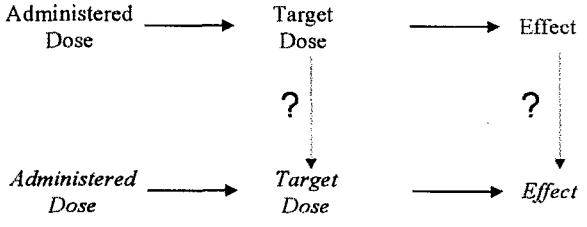
Uncertainties Due to Potential Species Differences

Rat



Human

ADME studies

Mechanistic / Sensitivity Studies
1. Adult
2. Developmental

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Mechanistic Studies

- Aid to quantitative interspecies extrapolation - basis to extend PBPK model
- Additional developmental studies to evaluate thyroid TH in fetal and post-natal periods
- Determine relative sensitivity of fetal/postnatal thyroid versus adult
- Determine relative sensitivity of rat versus human

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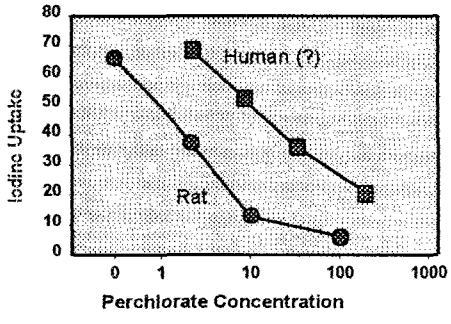
Resolving Uncertainties Mechanistic Studies

Do species differences exist?

compare rodent and human sensitivities using in vitro techniques



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Uncertainties in Risk

2. Age-Dependent Sensitivity
   Developmental effects can be permanent.
   Is the developing organism more sensitive?

Yes - need to carefully characterize

No - protection of maternal compartment

National Health and Environmental Effects Laboratory

ADME study

- Literature review of perchlorate discharge test
- Protocols proposed to evaluate perchlorate kinetics, iodine inhibition kinetics and thyroid hormone homeostasis
- Basis for development of physiologically-based pharmacokinetic (PBPK) model

National Health and Environmental Effects Laboratory

Resolving Uncertainty - Example

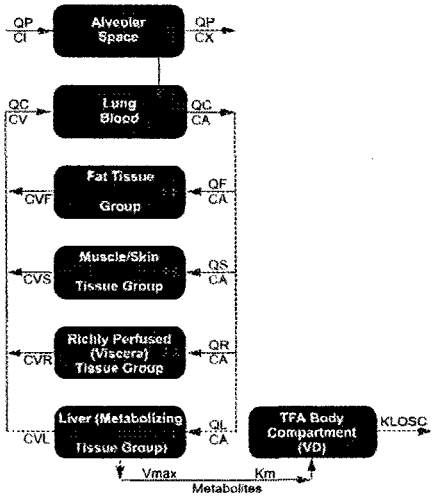
2. Age-Dependent Sensitivity

Determine relative sensitivity of fetal/postnatal thyroid versus adult

Determine relative sensitivity of rat versus human

National Health and Environmental Effects Laboratory

PBPK Model Schematic



National Health and Environmental Effects Laboratory

Summary

- Facts:
  - Perchlorate cause hypothyroidism
- Uncertainties
  - Animal to Human extrapolation
  - Age-dependent senstivity

National Health and Environmental Effects Laboratory

Development, QA/QC and Status of Study Protocols

David R. Mattie, PhD, DABT
Operational Toxicology Branch
AFRL/HEST

Perchlorate Stakeholders Forum
Sponsored by the IPSC
Henderson, NV
19-21 May 1998

Outline

- Development of Study Protocols
- QA/QC Procedures
- Status of Studies

Outline

- Development of Study Protocols
- QA/QC Procedures
- Status of Studies

May 1997 Perchlorate Study Protocol Review Meeting

- Expert Peer Review Panel:
  - Bring together the experts to determine what toxicology studies need to be conducted
  - Discuss protocols for 90-day and developmental neurotoxicity studies
  - Discuss additional studies needed
  - Prioritize all studies without regard to funding

May 1997 Perchlorate Study Protocol Review Meeting

- Dr. Joe Brown, California EPA, Office of Environmental Health Hazard Assessment
- Dr. Dan Caldwell, Toxicologist, Belle Meade, NJ
- Dr. Dorothy Canter, U.S. EPA, Office of Solid Waste and Emergency Response
- Dr. Charles Capen, Ohio State University, Department of Veterinary Biomedicine
- Dr. John Christopher, California EPA, Department of Toxic Substances Control
- Dr. Marvin Friedman, Cytec Industries, Inc.

May 1997 Perchlorate Study Protocol Review Meeting

- Mr. Greg Harvey, U.S. Air Force, Wright-Patterson Air Force Base
- Ms. Annie Jarabek, U.S. EPA, National Center for Environmental Assessment
- Dr. David Morry, California EPA, Office of Environmental Health Hazard Assessment
- Dr. Marilyn Underwood, California Department of Health Services
- Dr. David R. Mattie, AFRL, USAF

May 1997 Perchlorate Study Protocol Review Meeting Outcomes

- Prioritized list of 8 studies
- Agreement to continue as reviewers to develop and refine study protocols
- All final protocol information to be made available to the public through use of the world-wide-web on TERA's site
- Add reviewers and experts as needed

TOXICITY STUDIES
Recommended List:

- 1. 90-Day Subchronic Study
- 2. Developmental neurotoxicity Study
- 3. Genotoxicity assays
- 4. Mechanistic
- 5. ADME - Absorption, Distribution, Metabolism and Elimination
- 6. Developmental Study
- 7. 2-Generation Reproductive Study
- 8. Immunotoxicity

Protocol Review Team (as of 12 Jan 98)

- Dr. Joe Brown, California EPA, Office of Environmental Health Hazard Assessment (OEHHA)
- Dr. Dan Caldwell, Toxicologist, Belle Meade, NJ
- Dr. Dorthy Canter, US EPA (OSWER)
- Dr. Charles Capen, Ohio State University
- Dr. John Christopher, California EPA, DTSC
- Dr. Eric Clegg, US EPA (NCEA)
- Dr. Kevin Crofton, US EPA National Health and Environmental Effects Research Laboratory (NHEERL)
- Dr. Vicki Dellarco, US EPA (OW)

Protocol Review Team (as of 12 Jan 98)

- Dr. Marvin Friedman, Cytec Industries, Inc
- Mr. Greg Harvey, USAF, Wright Patterson AFB
- Ms. Annie Jarabek, US EPA (NCEA)
- Mr. Kevin Mayer, US EPA (Region IX)
- Dr. David Morry, California EPA (OEHHA)
- MaryJane Selgrade, US EPA (NHEERL)
- Dr. Marilyn Underwood, California Department of Health Services
- Ms. Brenda Pohlmann, Nevada Division of Environmental Protection

Status of Study Protocols

- 6 out of 8 are in progress
- Mechanistic and kinetic protocols are still being developed

Outline

- Development of Study Protocols
- QA/QC Procedures
- Status of Studies

QA/QC Procedures
Air Force Sponsored Studies

- Contract lab delivers draft report to AFRL for review by contract monitor and project director
- Review includes:
  - QA/QC to confirm study conducted according to protocol requirements
  - Contractual review for form and contract requirements

QA/QC Procedures
Air Force Sponsored Studies

- Comments returned to contract lab
  - Editorial, contractual, format
- Contract lab addresses comments
- Final draft to AFRL for technical review by Senior Scientist and associates with necessary expertise
- Contractor addresses final comments

QA/QC Procedures
Air Force Sponsored Studies

- Final report delivered to AFRL
- Final report delivered to EPA/NCEA within 48 hours
- Total review time: 45 days

QA/QC Procedures
PSG Sponsored Studies

- Contract lab delivers draft report to TERA/PSG for review by contract monitor
- Review includes:
  - QA/QC to confirm study conducted according to protocol requirements
  - Contractual review for form and contract requirements
  - Editorial, contractual, format

QA/QC Procedures
PSG Sponsored Studies

- Draft report undergoes technical review by AFRL
- Contractor addresses all comments
- Final report delivered to TERA/PSG
- Final report delivered to EPA/NCEA within 48 hours
- Total review time: 32 days

QA/QC Procedures Summary

- Standardized review process for all studies
- Technical review by AF Senior Scientist team
- Commitment to expedited review process to accommodate assessment schedule

Outline

- Development of Study Protocols
- QA/QC Procedures
- Status of Studies

TOXICITY STUDIES
Recommended List:

- 1. 90-Day Subchronic Study
- 2. Developmental neurotoxicity Study
- 3. Genotoxicity assays
- 4. Mechanistic
- 5. ADME - Absorption, Distribution, Metabolism and Elimination
- 6. Developmental Study
- 7. 2-Generation Reproductive Study
- 8. Immunotoxicity

1. 90-day subchronic study

- Guideline study: OPPTS 870.3100
- Added additional tests for:
  - Reproductive parameters
  - Mutagenic effects in bone marrow
  - Thyroid hormone levels
- Contract lab with necessary expertise
- Air Force collaboration
  - Stability study and dose verification
  - Hormone analysis

2. Developmental Neurotoxicity Study

- Guideline study: OPPTS 870.6300
  - Added thyroid histopathology of pups at day five
- Contract lab with demonstrated proficiency in this specialized study
- Air Force collaboration
  - Stability study and dose verification
  - Thyroid histopathology
  - Hormone analysis

3. Genotoxicity Assays

- Tests:
  - Ames Bacterial Mutation Assay (40 CFR 798.5265)
  - Mouse Lymphoma Assay (40 CFR 798.5300)
  - In vivo mouse bone marrow micronucleus test (40 CFR 798.5395)
- Contract lab with necessary expertise

4. Mechanistic

- Literature search for perchlorate discharge test by AFRL
- Studies proposed:
  - Effects of perchlorate in the developing animal
  - Iodine uptake
  - Biomarkers of Perchlorate Neurotoxicity
- By Neurotoxicity Division of USEPA NHEERL

5. ADME - Absorption, Distribution, Metabolism and Elimination

- Study protocols under development
  - Perchorate kinetics
  - Iodine inhibition kinetics
- By Air Force toxicology lab

6. Developmental Study

- Guideline study: OPPTS 870.3700
- Additional groups added to study
- Added hormone analysis and thyroid histopathology
- Contract lab with expertise

7. 2-Generation Reproductive Study

- Guideline study: OPPTS 870.3800
- Added analysis of thyroid hormones and histopathology of thyroids at additional timepoints
- Contract lab with necessary expertise

8. Immunotoxicity

- Incorporated aspects of guideline study (OPPTS 870.7800) to address concerns for perchlorate
- Proposed by Air Force Post Doc
- At Medical University of South Carolina
- Air Force collaboration

TOXICITY STUDIES
Recommended List:

- 1. 90-Day Subchronic Study
- 2. Developmental neurotoxicity Study
- 3. Genotoxicity assays
- 4. Mechanistic
- 5. ADME - Absorption, Distribution, Metabolism and Elimination
- 6. Developmental Study
- 7. 2-Generation Reproductive Study
- 8. Immunotoxicity

Report Status

- Final and interim reports will be sent to NCEA/EPA for assessment and the setting of the revised RfD

Report Status

- Final Reports available for EPA assessment:
  - 1. 90-Day (Spring 98)
  - 2. Developmental neurotoxicity study (Spring 98)
  - 3. Genotoxicity assays (Summer 98)
  - 6. Developmental study (Summer 98)

Report Status

- Interim reports available for EPA assessment:
  - 5. ADME - Absorption, Distribution, Metabolism and Elimination (Summer 98)
  - 7. 2 Generation reproductive (Summer 98)
  - 8. Immunotoxicity (Summer 98)

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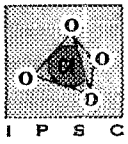
Development of the Revised Reference Dose / Risk Assessment

Annie M. Jarabek
National Center for Environmental Assessment
U.S. Environmental Protection Agency

Perchlorate Stakeholders Forum
Sponsored by the IPSC
Henderson, NV
19-21 May 1998



Outline

- EPA risk assessment guidelines
- NCEA perchlorate toxicity assessment team
- Revised RfD / risk assessment process

Recommended Studies

- 90-Day subchronic bioassay
- Developmental neurotoxicity study
- Genotoxicity assays
- Mechanistic studies
- ADME - Absorption, Distribution, Metabolism and Elimination
- Developmental study
- 2-Generation reproductive toxicity study
- Immunotoxicity

EPA Risk Assessment Guidelines

- Principles and procedures to frame the conduct of risk assessments
- Promote consistency and technical quality of scientific inferences
- Flexible, full consideration to all relevant scientific information case-by-case
- Revised as experience and scientific consensus evolve

EPA Risk Assessment Guidelines

- Developmental toxicity (1991)
  FR 56(234): 63798 - 63826
- Reproductive toxicity (1997)
  EPA No. EPA/630/R-96/009a
  NTIS PB97-100093
- Neurotoxicity (1998)
  EPA No. EPA/630/R-95/001Fa
  NTIS PB98-117831
- Thyroid follicular cell tumors (1998)
  EPA/630/R-97-002

EPA Risk Assessment Guidelines

- Proposed revision to carcinogenicity (1996)
  EPA/600/P-92/003C
  NTIS PB96-157599
- Exposure (1992)
  FR 57 (104): 22888 - 22938
- Chemical mixtures (1986) / Proposed 1998

Guidelines Available

- http://www.epa.gov/ncea
- EPA ORD publications, Technology Transfer and Support Division, NRML Phone: 513.569.7562; FAX: 513.569.7566. Need the EPA No.
- National Technical Information Service (NTIS): 703.487.4650; FAX: 703.321.8547. Need the NTIS PB No.

NCEA Perchlorate Toxicity Risk Assessment Team

• Harlal Choudhury	NCEA	general toxicology / risk assessment
• Eric Clegg	NCEA	reproductive toxicology
• Kevin Crofton	NHEERL	neurotoxicology
• Vicki Dellarco	OW	genetic toxicology
• Annie Jarabek	NCEA	general toxicology / dosimetry / risk assessment
• Gary Kimmel	NCEA	developmental toxicology
• MaryJane Selgrade	NHEERL	immunotoxicology

Toxicity Study Review and Revised RfD / Risk Assessment

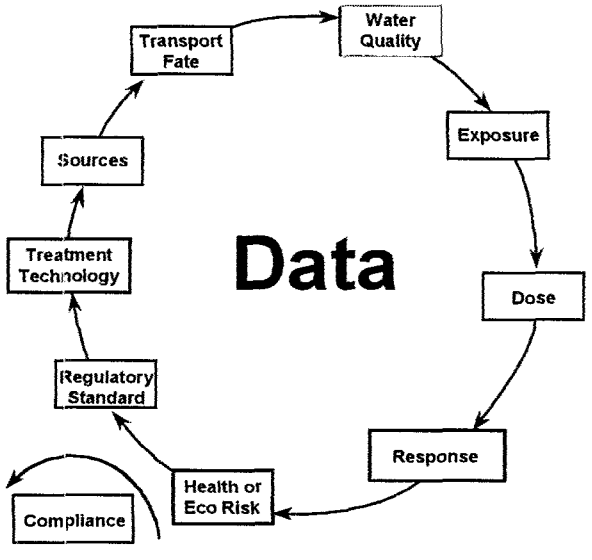
- Review of existing and new toxicity data
- Hazard identification
- Dose-response evaluation
  - Designation of effect levels (mathematical modeling or NOAEL / LOAEL procedure)
  - UF assignment
  - Uncertainty characterization - confidence statements

Revised RfD / Risk Assessment Review Process

- Internal peer review (September 1998)
- External peer review (October 1998)
- Response / revisions subsequent to external peer review (November 1998)
- Submit final revised RfD / risk assessment to Integrated Risk Information System (IRIS) process
- Refine as required with new data

Future Applications of Revised RfD

- Basis for various guidance levels (e.g., Health Advisory, NPDWR, Superfund remediation goals)
- Converted through the use of standard ingestion and body weight parameters (e.g., 2 L / day and 70 kg for adult)



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Peer Review of Perchlorate Risk Assessment

Peter Grevatt, Ph.D., U.S. EPA HQ

Presentation Goals

- Define Peer Review
- EPA Peer Review Policy
- Purpose of Peer Review
- Scope of Peer Review for Perchlorate
- Impact on Perchlorate Risk Assessment

Define Peer Review

- *"Documented critical review of Agency scientific or technical work product"*
  - In-depth Assessment
  - Conducted by qualified individuals
  - Independent of those who performed work
  - Equivalent in technical expertise

EPA Peer Review Policy

- *"Major scientifically and technically based work products related to Agency decisions should be peer reviewed..."*

- *"For those work products that are intended to support the most important decisions or that have special importance in their own right, external peer review is the procedure of choice..."*

Purpose of Peer Review

- Ensure quality, credible Agency decisions
- Preparation of sound, technically defensible analyses and work products.

Scope of Perchlorate Peer Review

- Independent, external peer review of all aspects of the perchlorate risk assessment
- EPA Office of Solid Waste and Emergency Response will oversee peer review
  - Study protocols
  - Study results
  - Development of reference dose
    - Selection of critical endpoint
    - Use of uncertainty factors
    - Risk characterization

Scope of Perchlorate Peer Review

- Stakeholder participation
  - Nomination of expert peer reviewers
    - -- Selection by independent scientific panel
    - -- Examination of potential conflict of interest
  - Open peer review panel meeting
  - Opportunity for comment by interested parties
  - Preparation of final peer review report

Impact on Perchlorate Risk Assessment

- Submit Final Peer Review Report to NCEA
- Preparation of Responsiveness Summary
  - Detailed response to all peer review comments
    - -- Comments addressed
    - -- Explanation of Changes
- Completion of final risk assessment

Where to reach me!

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grevatt.peter@epa.gov

The Safe Drinking Water Act and Perchlorate

MIKE OSINSKI
Office of Ground Water and Drinking Water
U.S. Environmental Protection Agency
Washington, D.C.
202-260-6252
202-260-3762 (fax)
OSINSKI.MICHAEL@epamail.epa.gov

Contaminant Identification and Selection Under the SDWA

- **Contaminant Selection Under the 1986 Amendments to SDWA:**
  - ⇨ Regulate 83 contaminants by 1989;
  - ⇨ Regulate 25 contaminants every 3 years.
- **Congress, EPA had Implementation Concerns:**
  - ⇨ Missed statutory deadlines;
  - ⇨ Water systems encountered difficulty in timely compliance;
  - ⇨ Focus on sound science and contaminants posing greatest risk.

Contaminant Identification and Selection Under the SDWA

- **Contaminant Selection Under the 1996 Amendments to SDWA.**
  - ⇨ Publish a Contaminant Candidate List (CCL) of contaminants known or anticipated to occur in DW and not subject to NPDWRs by Feb 1998.
  - ⇨ Broad consultation with stakeholders, NDWAC, and SAB.

Contaminant Identification and Selection under the SDWA

- **Draft CCL Published on Oct 6, 1997.**
  - ⇨ Did not include perchlorate, but sought comment on whether to include it on the final CCL.
  - ⇨ Public comments indicated overall support for adding perchlorate to the CCL.
- **Final CCL published on March 2, 1998.**
  - ⇨ Contains 50 chemical and 10 microbiological contaminants.

Contaminant Candidate List (CCL)

- **Functions of the CCL:**
  - ⇨ Make determinations for at least 5 contaminants of whether or not to regulate with a NPDWR by 2001.
  - ⇨ Focus and prioritize research agenda for contaminants with data gaps.
  - ⇨ Source for selection of contaminants for unregulated contaminant monitoring regulation (UCMR) due in 1999.

Perchlorate and the CCL

- **Two categories of contaminants on the CCL:**
  - ⇨ (1) Regulatory Determination Priorities;
  - ⇨ (2) Research Priorities.
- **Perchlorate falls into the research priorities category due to extensive data gaps in:**
  - ⇨ Occurrence; health effects, treatment technologies, and analytical methods research.

Regulatory and Policy Agenda for Perchlorate

- **Determination to regulate not likely by 2001.**
  - ⇨ Extensive data gaps in all areas.
- **EPA is not currently planning to include perchlorate as a contaminant in the proposed UCMR (Fall 1998).**
  - ⇨ Lack of EPA approved analytical method(s).
  - ⇨ Recommend near-term special occurrence studies.

Next Steps for Perchlorate

- **Perchlorate is a research and occurrence priority for the OGWDW.**
  - ⇨ In process of developing short and longer term research plans on health, treatment, and analytical methods.
- **OGWDW is very engaged in the IPSC.**
  - ⇨ Ensure exchange of scientific information to support decision making based on sound science and stakeholder involvement.

Next Steps for Perchlorate

- **Possible Scenarios:**

(1) Longer Term (3 to 5 years):

⇨ Data gaps filled and perchlorate moves to the regulatory determination priority category of next CCL -- due in 2003.

(2) Near Term (1-2 years):

⇨ If health effects and occurrence data warrant, develop a Health Advisory.

EPA Health Advisory Program

- **SDWA General Authority:**

⇨ "The Administrator may publish health advisories (HA), which are not regulations, or take other appropriate actions for contaminants not subject to any national primary drinking water regulation."

- **HAs represent concentrations of contaminant in drinking water which adverse health effects are not expected to occur.**

EPA Health Advisory Program

- **Not federally enforceable.**
- **Subject to change as new information becomes available.**
- **Can serve as technical guidance to assist State, Tribal, and local officials responsible for protection of public health.**

EPA Health Advisory Program

- **HAs used in emergency situations and describe concentrations of a contaminant at which adverse non-carcinogenic effects are not anticipated to occur following exposures:**
  - 1-day
  - 10-day :
  - Longer term (i.e. 7 years)
  - Lifetime

Sample HA Calculations

- **Determine RfD in mg/kg/day.**
- **Determine DWEL (Drinking Water Equivalent Level) in mg/L, assuming 100% drinking water contribution.**
- **Determine HA in mg/L.**

Sample HA Calculations

- ~~DWEL (mg/L) = (RfD)(70 kg adult)*~~
  ~~(2 L/day)~~

  DWEL (mg/L) = (RfD)(10 kg child)**
  (1 L/day)

* *for lifetime HA*

** *for 1 day, 10 day, and longer term HA*

- HA (mg/L) = (DWEL)(% DW contribution)

Ecological Impact/Transport and Transformation of Perchlorate

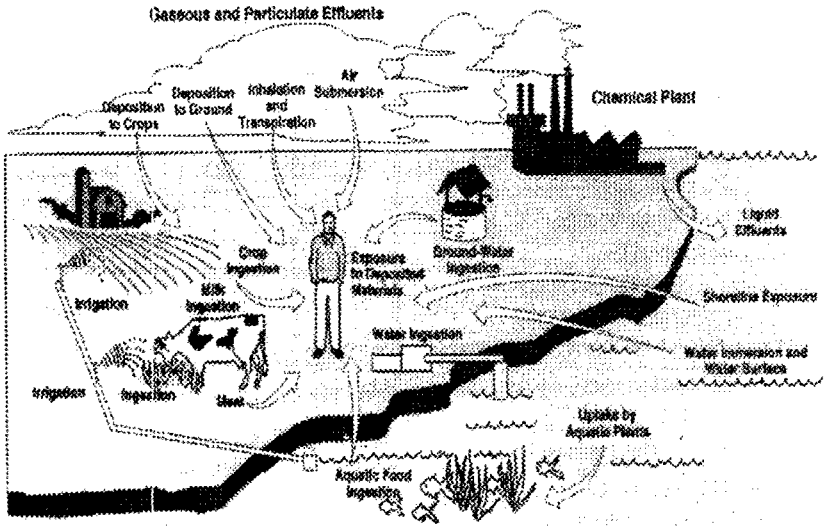
Mr. Cornell Long, USAF
Dr. Ron Porter, USAF
Dr. Mark Sprenger, USEPA
Dr. Clarence Callahan, USEPA

Introduction

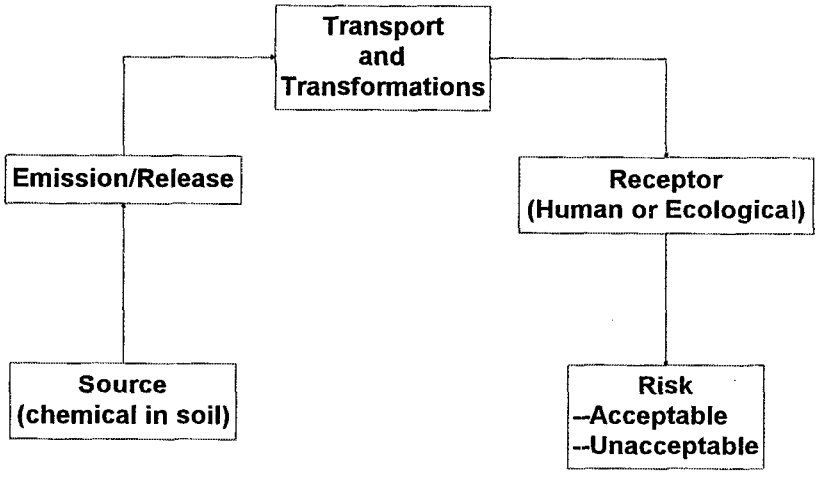
- Background
- Fate and Transport of perchlorate
- Historical Studies
  - Potential ecological receptors
  - Observed Effects
- Proposed Activities and EPA Framework
- Discussion

Background

- Perchlorate salts have low volatility, but high solubility
- Solubility leads to high mobility in aqueous systems
  - Surface water
  - Groundwater
- Mobility and persistence may pose a threat to ecological receptors



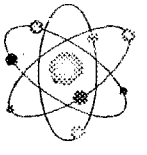
Exposure Model



Fate and Transport

(Transport and Transformation)

- What happens to perchlorate in the environment?
  - Physical characteristics
  - Attenuation processes
- What are the data gaps?



Physical Characteristics

- Vapor Pressure--no values found in literature
  - Volatilization not expected to be predominant pathway
- Density--1.95 g/mL
  - Will sink in water
  - Concentrated solutions also more dense than water

Physical Characteristics

- Solubility--20.2 g/100g solution
  - Dissolution expected and perchlorate ion will predominate in solution
  - Potential for potassium salt to precipitate--function of ion concentrations
- Standard potential--reduction for Cl from +7 oxidation state to -1
  - All values positive which indicates the reaction is thermodynamically favored

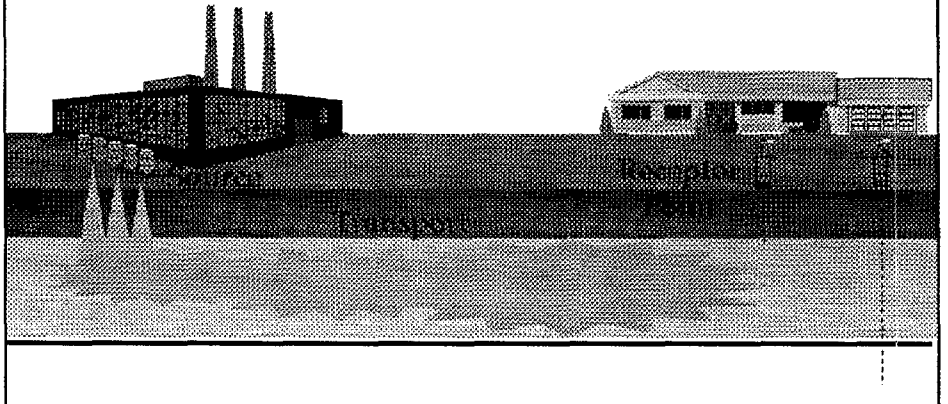
Physical Characteristics

- Standard potential

$$ClO_4^- + 4H_2 \longrightarrow 4H_2O + Cl^-$$

  - Little evidence that reaction occurs spontaneously
  - Reduction rate negligible at room temperature
  - Conclusion: Perchlorate is kinetically stable (most stable oxo-compound of chlorine)

Mobility of Perchlorate



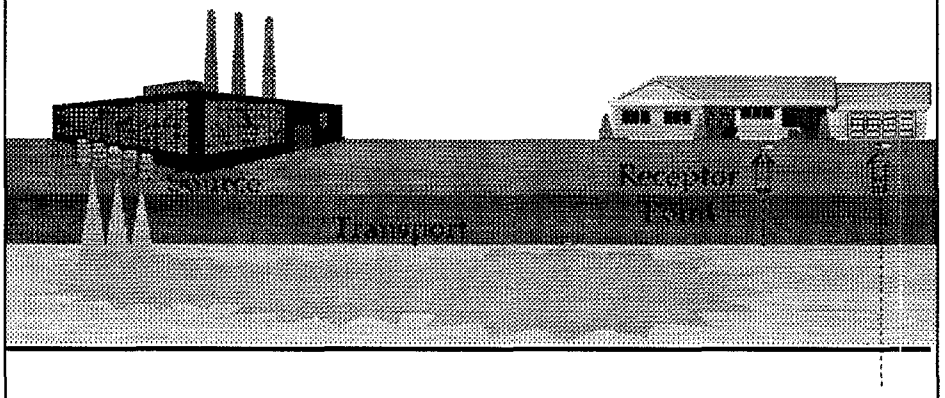
Attenuation Processes

- Dilution
- Precipitation
- Biological or chemical reduction
- Adsorption
- Ion-exchange

Attenuation Processes

- Dilution--concentrations expected to be significantly lower away from the source
  - However, function of the inert binder may influence source area concentrations
- Precipitation
  - Potassium less soluble, could lead to subsurface precipitation; long-term source area, near source area, and far source area re-dissolution

Mobility of Perchlorate



Attenuation Processes

- Biological or chemical reduction
  - Perchlorate reduction can occur at metal surfaces under acidic pH; however, inhibition by competing anions a problem
- Sorption
  - Perchlorate absorbs weakly to most soil minerals (NO_3^- and Cl^- more favorable)
  - Minimal impact inhibiting mobility

Summary

- Perchlorate is very soluble
- Very stable at low concentrations
- Very inert ion
- Some potential for precipation in subsurface
- Reduction and sorption occurs to a lesser extent

Data Gaps General

- Binder Effects
  - Binder chemical degradation rates?
  - Leachability from binder?
  - Concentration of binder + other contaminants?
- Role of reduction and interaction of ClO_4 with subsurface soils

Data Gaps
Site-Specific

- Soil properties
- Hydrology
- Infiltrating groundwater
- Characterization of leachates produced from source and near source soils

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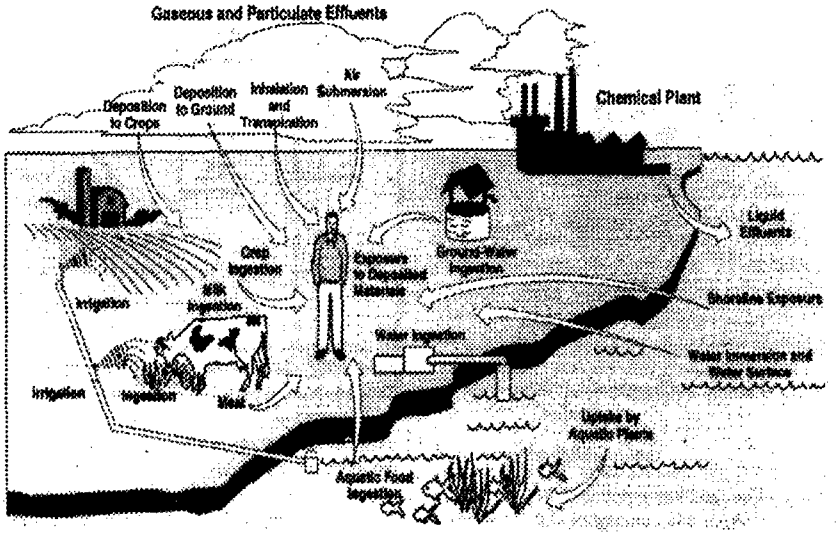
Historical Studies of Perchlorate Effects

Dr. Ron Porter
Ecological Toxicologist
Human Systems Center
Brooks AFB, TX



Ecological Receptors

- Aquatic biota
  - Sediment organisms
  - Aquatic plants
  - Aquatic vertebrates (fish)
  - Aquatic invertebrates (clams, crayfish, etc.)

Ecological Receptors (cont)

- Terrestrial biota
  - Soil organisms
  - Terrestrial plants
  - Terrestrial vertebrates (birds, mammals,etc.)
  - Terrestrial invertebrates (insects, spiders, etc.)

Ecological Receptors (cont)

- Agricultural products
  - Row crops
  - Livestock
  - Commercial fishing
- Food chain concerns
  - Recreational fishing
  - Fruits and nuts
  - Home gardens

Results of Data Search
AP Acute Effects-Aquatic

- Ammonium perchlorate
  - Bacteria 100-1870 ppm (effect)
  - Algae 100 ppm (no effect)
  - Hydra 350-600 ppm (effect)

Results of Data Search
AP Acute Effects-Terrestrial

- Corn (growth) 1-1000 ppm (effect)
- Cotton (seeds) 55 g/sq.m. (effect)
- Ryegrass (seeds) 55 g/sq.m. (effect)
- Soybean (growth) 1-1000 ppm (effect)
- Wheat
  - seeds 0.1-1000 ppm (effect)
  - growth 10 ppm (effect)

Data on Other Perchlorates

- Potassium perchlorate
  - Algae 79-360 ppm (effect)
  - Protozoan 23-1117 ppm (effect)
  - Daphnia 82-670 ppm (effect)
- Sodium perchlorate
  - Fish 3000-7000 ppm (effect)
  - Soybean 2.5-30 ppm (effect)

Data on Other Perchlorates (cont)

- Nitronium perchlorate
  - Fish 100-200 ppm (no effect)
  - Squash, peanut, corn 1000 ppm (no effect)

Results of Data Search
Chronic Effects

- No data for effects of ammonium perchorate on terrestrial or aquatic plants and animals were found in the literature.
- Limited data for effects of potassium perchlorate were found in the literature
  - Two studies on the thyroid of lampreys
  - One study on growth and productivity of soybeans

Problem

What appropriate species of animals and plants and what assays are appropriate to evaluate potential ecological effects from exposure to ammonium perchlorate?

Contact

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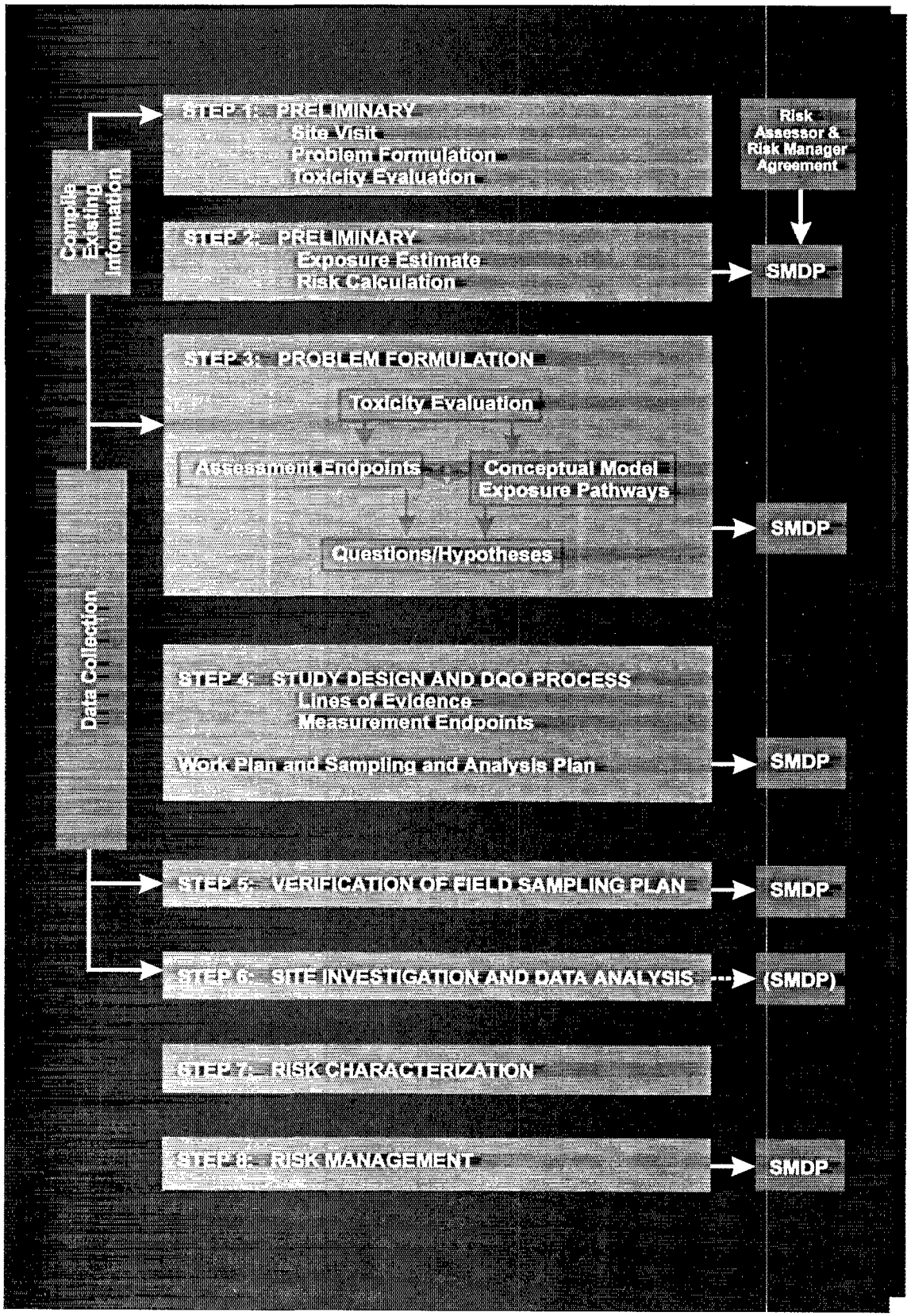
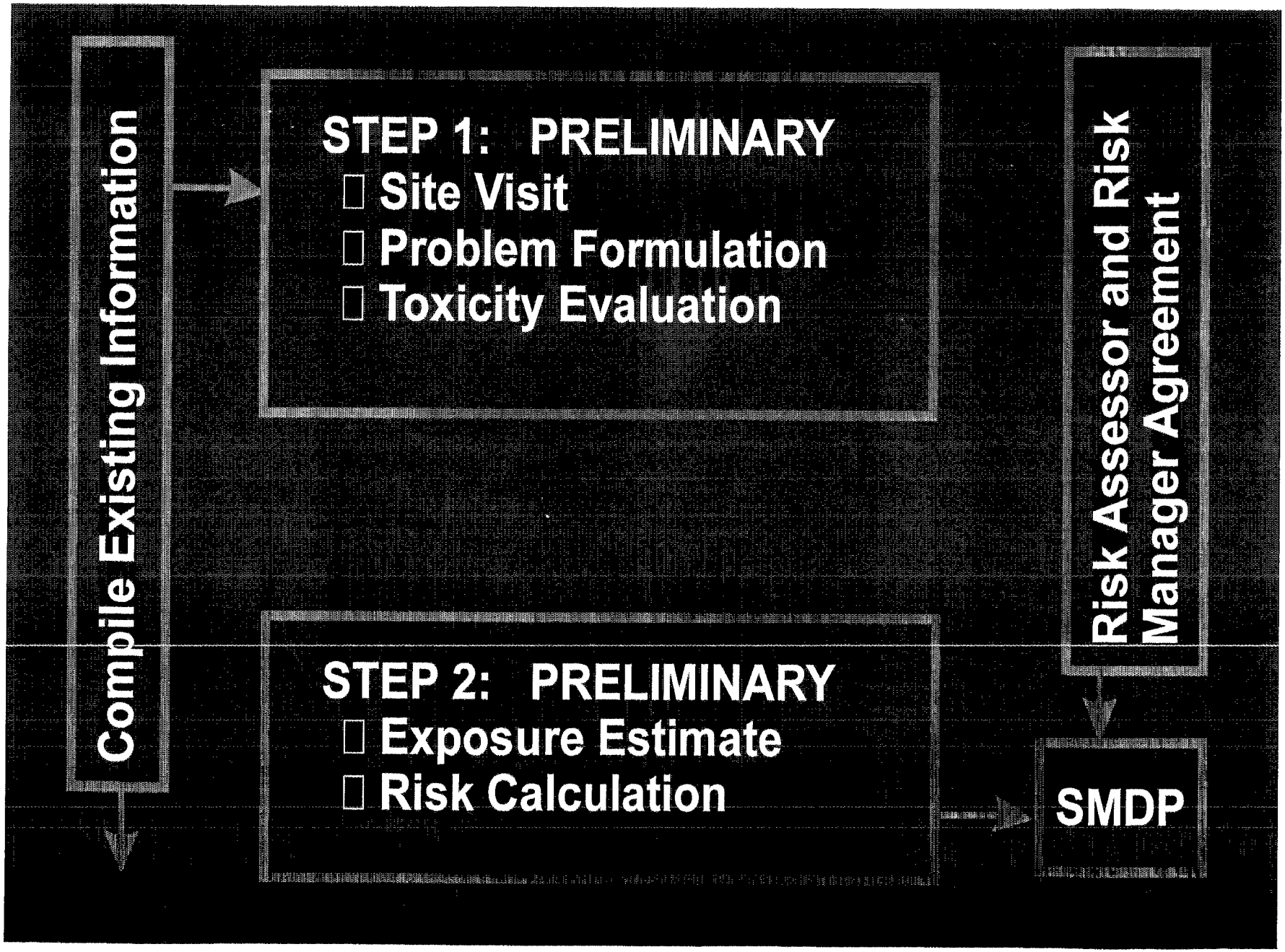
Perspective on the Process and Issues of Ecological Risk Assessment on Perchlorate

Mark D. Sprenger, Ph.D
USEPA OERR-ERTC

Clarence Callahan
USEPA-Region IX

The U.S. EPA Office of Emergency and Remedial Response (OERR), I.e. Superfund, has adopted a process for designing and conducting ecological risk assessments on chemical stressors at hazardous waste sites.


STEP 1 PRELIMINARY
Site Visit
Problem Formulation
Toxicity Evaluation
Risk Assessor & Risk Manager Agreement
Compile Existing Information
STEP 2 PRELIMINARY
Exposure Estimate
Risk Calculation
SMDP
STEP 3 PROBLEM FORMULATION
Toxicity Evaluation
Assessment Endpoints
Conceptual Model
Exposure Pathways
Questions/Hypotheses
SMDP
Data Collection
STEP 4 STUDY DESIGN AND DQO PROCESS
Lines of Evidence
Measurement Endpoints
Work Plan and Sampling and Analysis Plan
SMDP
STEP 5 VERIFICATION OF FIELD SAMPLING PLAN
SMDP
STEP 6 SITE INVESTIGATION AND DATA ANALYSIS
(SMDP)
STEP 7 RISK CHARACTERIZATION
STEP 8 RISK MANAGEMENT
SMDP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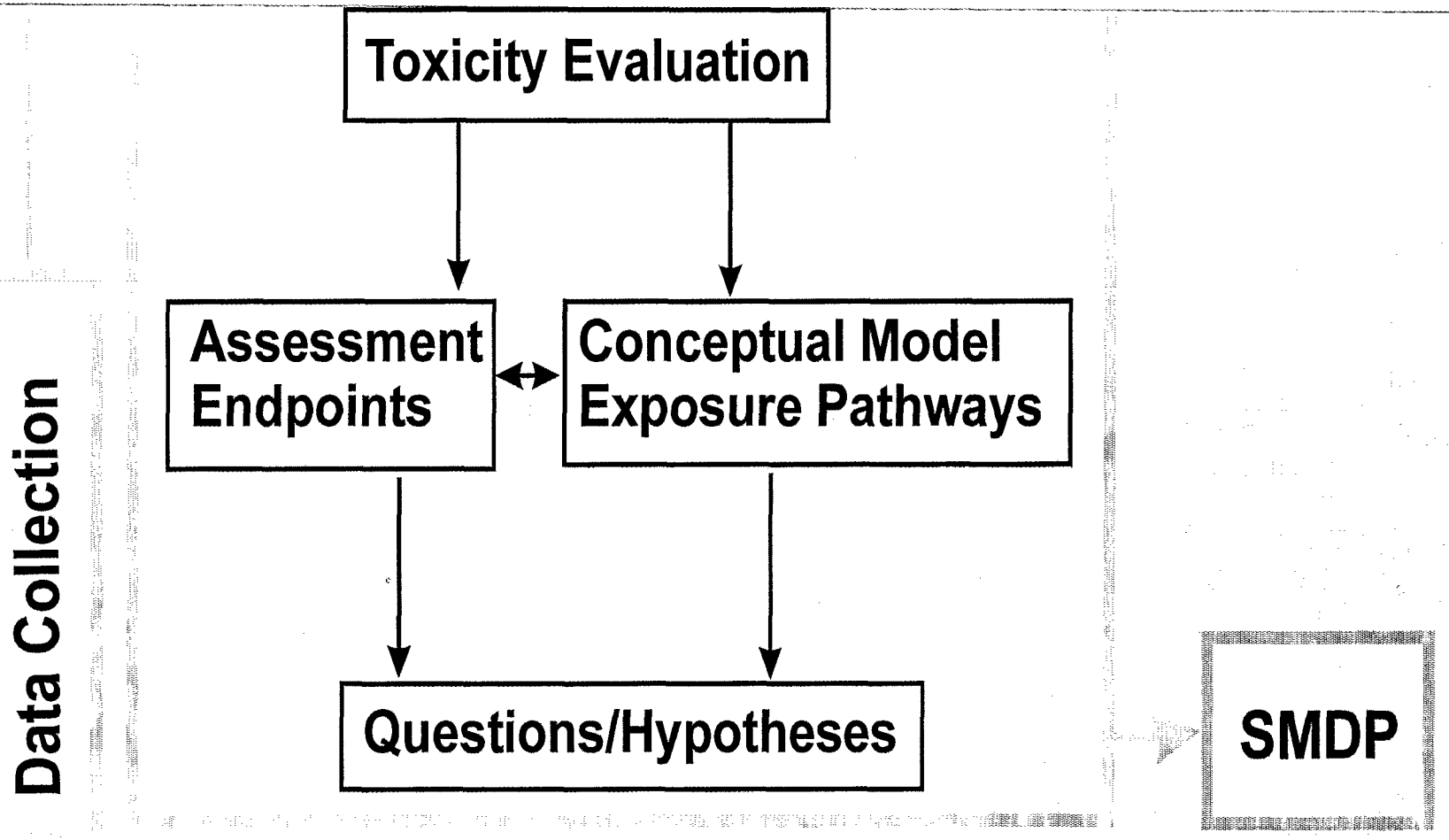
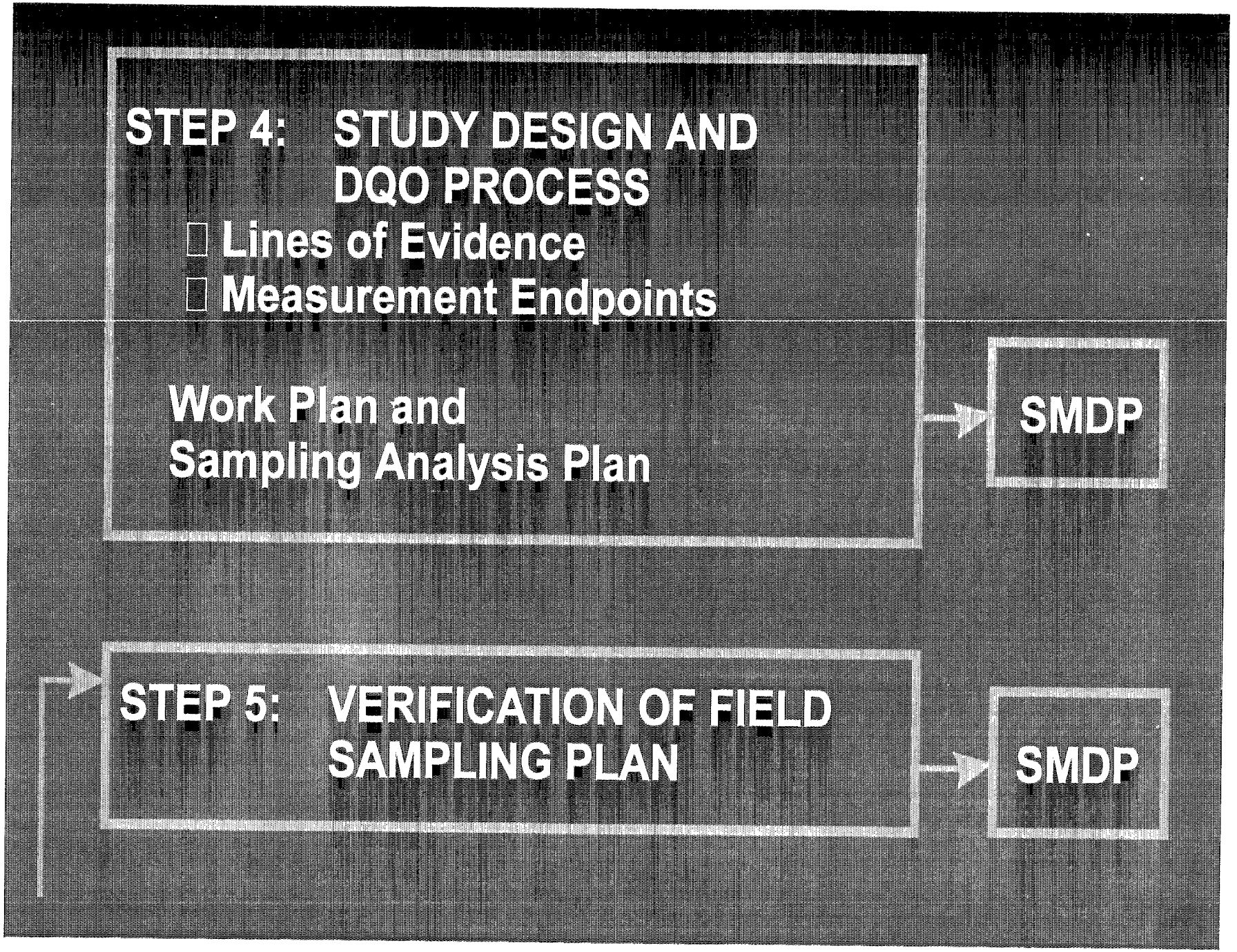
STEP 3: PROBLEM FORMULATION

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SMDP
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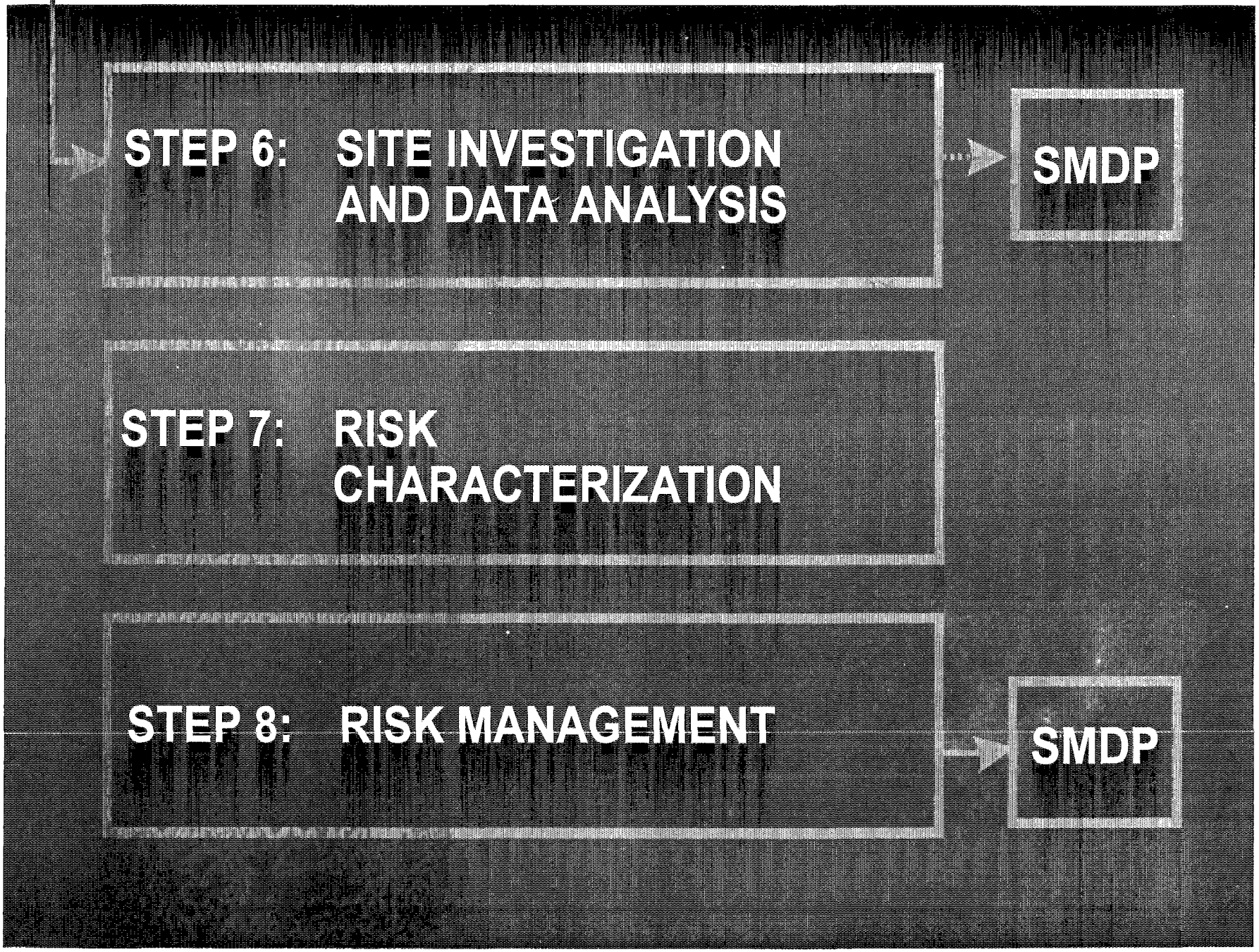
SMDP


STEP 6: SITE INVESTIGATION AND DATA ANALYSIS
SMDP
STEP 7: RISK CHARACTERIZATION
STEP 8: RISK MANAGEMENT
SMDP

The heart of an ecological risk assessment is problem formulation. An effective problem formulation depends upon knowledge of contaminant fate and transport and either mechanism of toxicity and/or sensitive species

We know perchlorates:

- can affect mammalian and amphibian thyroid functioning
- can affect fish at high water concentrations
- can affect freshwater invertabrates at high water concentrations
- can affect plants

However, mechanism of toxicity is unknown

Outstanding issues which are needed to do a comprehensive problem formulation include:

- further understanding of environmental fate and transport of perchlorate at low levels in environmental settings
- knowledge of perchlorate bioaccumulation potential and possible sequestering within organisms
- knowledge of possible toxicity mechanisms other than thyroid functioning
- evaluation of exposure mechanisms for ecological receptors

What are the current sources of additional information?

- Analytical Techniques
  - limit the ability to evaluate bioaccumulation
  - limit the ability to evaluate sequestering in organisms
  - limit ability to evaluate exposure
- Use of high exposure toxicity tests at low exposure toxicity

In Conclusion:

- The current approach to developing data on the ecological risks from perchlorate have conceptually followed Superfund's ecological risk assessment process.
- Because of the substantial knowledge and analytical limitations which currently exist, careful planning and a diligent problem formulation are critical to the successful evaluation of any potential ecological risk from perchlorate.

Historical Background on Analytical Techniques

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IPSC
Analytical Methods Sub-Committee

Co-Chairs

Steve Pia, USEPA-NERL

David Tsui, AFRL/HEST

Howard Okamoto, CA DHS

Sanwat Chaduri, UDOH/DELS

Analytical Techniques For Perchlorate Analysis

- Gravimetric Analysis – Ion Pair Extraction
  - Nitron
  - Methylene Blue
  - Brilliant Green, etc.
- UV-Spectrometry
- Flame Atomic Absorption Spectrometry
- Ion Chromatography

Disadvantages of Non-IC Methods

- Lack of Selectivity
- Lack of Specificity
- Lack of Sensitivity

Perchlorate IC Methods

- Pre-Jan 1997
  - Aerojet Method
  - MDL = 100 ppb
- April 1997 to Jan 1998 - CDHS Method
  - MDL = 4 ppb
  - 45 Laboratories were contacted
  - 23/45 Labs were using CDHS
- Jan - May 1998 - Dionex AS-11 Method
  - Dionex TechNote 121
  - MDL < 1 ppb
  - Published in AEL., 4/1998
  - 7/23 Labs have switched to AS-11

CDHS Users

Air Force Research Lab - Toxicology Laboratory

Dionex Corp.*

Metropolitan Water District of Southern California *

Thiokol *

UDOH - DELS *

Montgomery Watson Labs *

Advanced Technology Labs

Aerojet

APPL *

Alliant Technology Systems

Alpha Analytical

California DHS- Berkley

California DHS-Los Angeles

California Laboratory Services

Clinical Laboratory of San Bernardino, Inc.

Columbia Analytical Services

E. S. Babcock and Sons, Inc.

Air Force Research Lab - Environics Lab.

Los Angeles Agricultural Commission-Environmental Toxicology Lab

Weck Laboratories, Inc.

AMPAC

Perchlorate Analysis by Ion Chromatography

The CA DHS Protocol

H.S. Okamoto, D.K. Rishi and S.K. Perera

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Disclaimer

- **Mention of trade names or commercial products does not constitute endorsement or recommendation for use.**

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Topics

- Equipment
- Eluent Composition Study
- Linear Calibration Range
- MDL Study
- Interferences
- Sample Collection and Preservation
- Method Performance
- Method Advantages
- Method Limitations
- Additional Needs

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Introduction

- Ammonium perchlorate (NH_4ClO_4) is freely soluble in water.
- Dilute solutions of perchlorate are very stable.
- Redox rate: $ClO^- > ClO_2^- > ClO_3^- > ClO_4^-$
- CA DHS provisional action level for perchlorate in drinking water is 18 ppb.

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Equipment

- **Ion chromatograph: autosampler, dual piston pump, ion suppressor, conductivity detector and data system.**
- **Sample loop: 740 µL (12′ x 0.02″ tubing)**
- **Column: Dionex IonPac® AS5 (4 x 250 mm)**
- **Chemical regenerant: Dilute sulfuric acid**
- **Eluent: 120 mM NaOH + 2 mM p-cyanophenol**

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Eluent Composition Study

- **High concentration of NaOH (120 mM) is employed in the eluent.**
- **p-Cyanophenol modifier must be added to the eluent to deactivate the AS5 ion exchange column.**
- **In initial tests, the p-cyanophenol concentration was varied while maintaining the NaOH concentration at 120 mM.**

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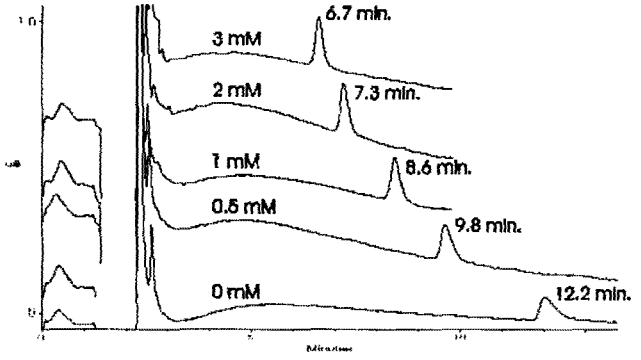
Effects of p-Cyanophenol on the Elution of ClO_4^-

- 15 ppb Perchlorate
- Eluent: 120 mM NaOH + X mM p-Cyanophenol



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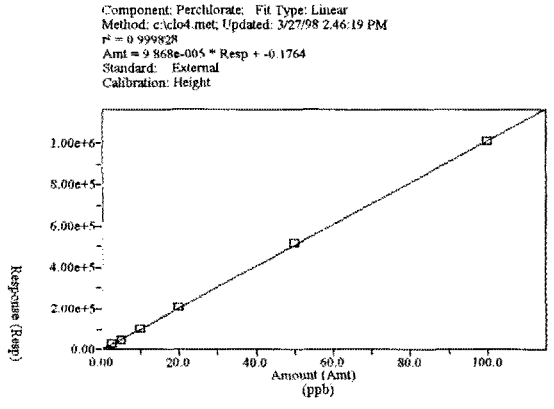
Linear Calibration Range

2.5 to 100 ppb Perchlorate



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MDL Study

ClO_4^- Spike Conc. (µg/L)	No. of Spiked Replicates	Mean Recovery (µg/L)	SD (µg/L)	Calculated MDL (µg/L)
2.5	16	2.3	0.12	0.8
4.0	16	3.9	0.11	0.7

Pooled MDL (df = 30)	0.7 µg/L
Reporting Limit (5 x MDL)	4 µg/L

ClO_4^- Spike Conc. (µg/L)	No. of Spiked Replicates	Mean Recovery (µg/L)	SD (µg/L)	RSD (%)
0	16	n/a *	n/a	n/a
1.0	16	0.8 **	0.4	50

* One false positive result of 0.7 µg/L.
** Includes 2 false negative results.

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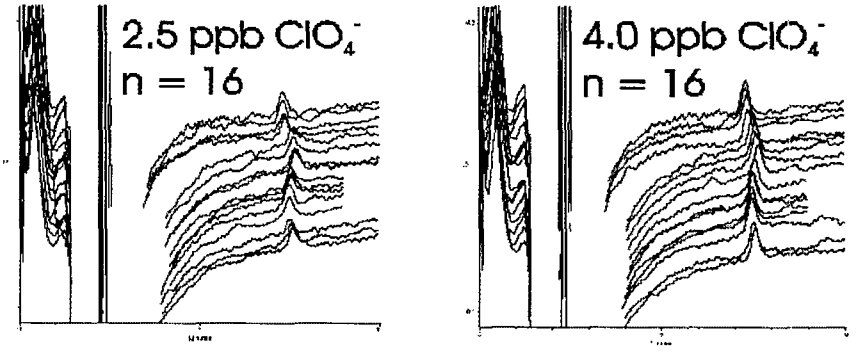
MDL Study



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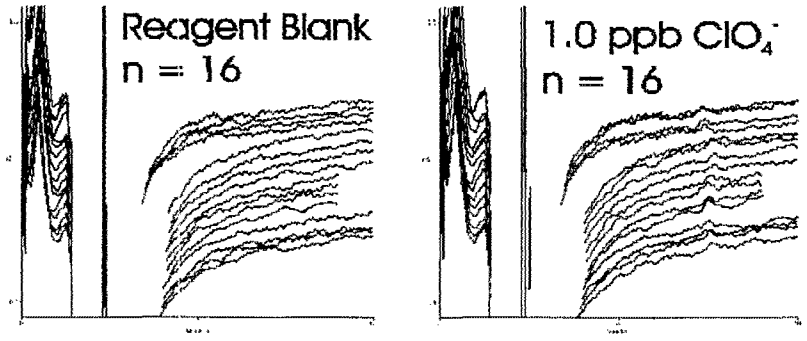
MDL Study



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Interferences

- **Pump noise (pressure pulses) - oscillating baseline.**
- **Air bubbles trapped in the pump head or conductivity cell -- baseline spikes and/or oscillating baseline.**
- **Improperly adjusted chemical suppression -- high background conductivity, low perchlorate response.**
- **Detergents and other organics -- column, suppressor and detector fouling.**
- **High sample TDS -- column and detector overload; may severely affect baseline response.**

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Anions Known Not to Colute with Perchlorate

Arsenate	Cyanide	o-Phthalate
Arsenite	Humic Acid	Selenate
Bromate	Iodate	Sulfate
Bromide	Iodide	Sulfite
Carbonate	Molybdate	Thiocyanate
Chlorate	Nitrate	Thiosulfate
Chloride	Nitrite	
Chromate	o-Phosphate	

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Sample Collection and Preservation

- Sampling container: HDPE plastic bottles
- Sample storage: store at 4°C
- Holding time: 28 days (likely to be more)

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Holding Time Study - Stored at 4°C

Well ID.	Date Collected	Conduct. µS/cm	Initial Hold: 6-11 Days	Holding Time 54 Days	Holding Time 70-71 Days
MAFB	3/25/97	120	ND		ND
#4MB	4/10/97	120	ND	ND	
SCWC	3/24/97	300	4.4		~3.9 (-11%)
#14	4/10/97	250	4.0	4.8 (+20%)	
SCWC	3/24/97	180	6.8		7.8 (+15%)
#19	4/10/97	300	7.6	7.7 (+1%)	
MAFB	3/25/97	120	14		15 (+7%)
#3MB	4/10/97	120	16	16 (0%)	
MAFB	3/25/97	120	67		68 (+1%)
#1MB	4/10/97	120	72	72 (0%)	
SCWC	3/25/97	260	260		250 (-4%)
#13	4/10/97	320	250	230 (-8%)	

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Holding Time Study

- **Tap water sample fortified with perchlorate**
  - **Stored for 10 months at 4°C**
  - **Stored for 10 months at room temperature**

Sample Conductivity	Initial ClO_4^- Conc.	Storage Temperature	ClO_4^- Conc. after 10 Months
840 µS/cm	18.1 ± 1.3 µg/L (n = 8)	4°C	19.3 ± 0.3 µg/L (n = 3)
		Room Temp.	19.4 ± 0.3 µg/L (n = 3)

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Method Performance

Single Operator Accuracy and Precision

Sample Type	Sample Matrix	ClO_4^- TV (µg/L)	No. of Repl.	ClO_4^- Mean Recovery (µg/L)	ClO_4^- Mean Recovery (%)	SD (µg/L)	RSD (%)
IPC	Reagent Water	5.0	105	5.1	102	0.4	7.2
		100	102	103	103	4.6	4.5
Alternate Source Material	Reagent Water	4.0	34	4.0	101	0.3	7.2
		15	3	15	100	1.2	8.0
		100	4	100	100	2.8	2.8
LFB	Reagent Water	4.0	54	4.1	102	0.3	8.3
		15	6	15	100	0.5	3.4

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Method Performance

- **Sample Duplicate Analysis & MS/MSD**
- **Single Operator Accuracy and Precision**

Sample Type	Sample Matrix	No. of Replicate Pairs	Mean RPD (%)	SD of Mean RPD (%)
Sample/Sample Duplicate: 4 to 260 µg/L of ClO4-	Groundwater	18	1.3	1.9

Sample Type	Sample Matrix	Spike Conc. (µg/L)	No. of Spiked Pairs	Duplicate Spike Mean Recovery (µg/L)	Duplicate Spike Mean Recovery (%)	Mean RPD (%)	SD of Mean RPD (%)
MS/MSD	Groundwater	4	47	4.1	103	7.7	6.1

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Inter-Laboratory Performance

- Tap Water
- Conductivity = 840 µS/cm
- ClO_4^- TV = 18.1 µg/L
- Acceptable Range: 14.3 - 21.9 µg/L

- No. of Labs = 11
- Mean Value Reported = 18.6 ± 1.8 µg/L

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Method Performance

- Capable of meeting the QC requirements in EPA 300.0 for ion chromatography:
  - QCS result within ± 10% of known value.
  - Instrument performance check solution results within ± 10% of calibration.
  - Method blank results less than the MDL.
  - Lab fortified blank results within control limits of 90 - 110%.
  - Laboratory fortified sample matrix recovery results within 80 to 120%.

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Method Advantages

- **Uses current technology that is available in many water utility and commercial analytical laboratories.**
- **Based on EPA 300.0 - many analytical laboratories are familiar with the QA/QC requirements.**
- **Requires very little sample preparation for drinking water samples.**
- **Quick and easy to perform.**
- **Provides the sensitivity required for the current California DHS provisional action level of 18 ppb in drinking water.**

April 1998 CA Department of Health Services - DDWEM/SRLB

Method Limitations

- **Requires a large sample volume of 740+ µL to achieve the necessary sensitivity.**
- **Due to the large sample volume, high TDS in a sample may cause interference in the detection and/or quantification for perchlorate at very low levels.**
- **High TDS in a sample may also cause column, suppressor, and/or detector fouling that can result in a noisy and unstable baseline.**
- **AS5 column activity causes perchlorate to tail without a modifier (p-cyanophenol) added to the eluent.**

April 1998 CA Department of Health Services - DDWEM/SRLB

Additional Needs

- Need for confirmatory procedures, including identification.
- Need for improved detection limits.
- Need for clean up methods.
- Need to keep method simple and transferable to water utility and commercial analytical laboratories.
- Need for a more comprehensive storage and holding time study.
- Need for a more comprehensive inter-laboratory performance study.

April 1998 CA Department of Health Services - DDWEM/SRLB

Acknowledgements

- D.K. Rishi and S.K. Perera, CA DHS
- F. Baumann, (retired) CA DHS
- W. Steeber and staff, CA DHS
- A. Fitchett and K. Anderson, Dionex Corp.

April 1998 CA Department of Health Services - DDWEM/SRLB

References

- Record 269, Dionex Chromatogr. Database 4.2.0, Dionex Corp.
- Haddad, P.R. & Jackson, P.E., Ion Chromatogr.: Principles and Applications, J. Chromatogr. Lib. 1990: 46:Ch. 4.
- CFR 40, Ch. 1, Part 136, Appendix B
- US EPA Method 300.0: Determination of Inorganic Anions by Ion Chromatography, Rev. 2.1, Aug. 93

Contact

Howard Okamoto
CA Dept. of Health Services - SRLB
2151 Berkeley Way
Berkeley, CA 94704

Ph. (510) 540-2205
email hokamoto@ix.netcom.com

April 1998 CA Department of Health Services - DDWEM/SRLB

An Improved Ion Chromatographic Method for Low Level Perchlorate Analysis

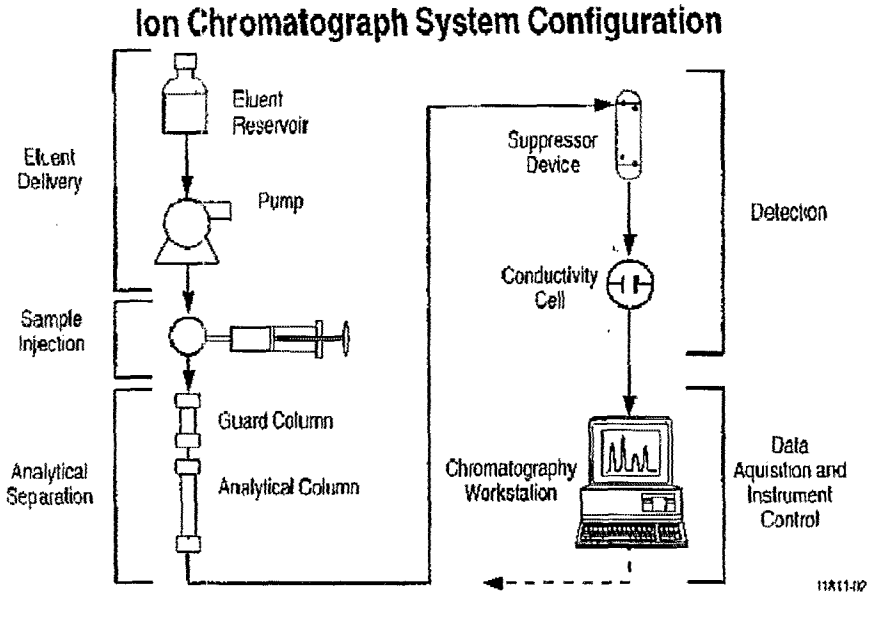
Peter E. Jackson, Ph.D.
Environmental Market Manager
Dionex Corporation
1228 Titan Way
Sunnyvale CA 94088-3606

PERCHLORATE - WHAT ARE THE ISSUES

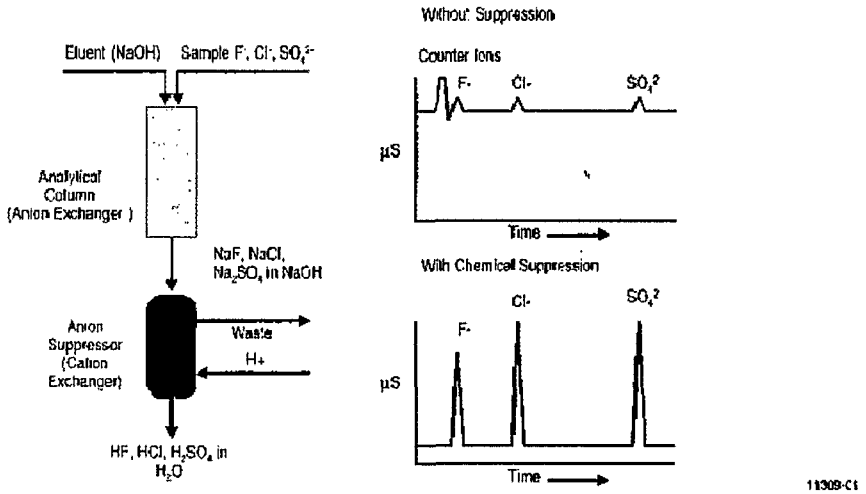
- Contamination found in CA, NV, UT & WV
- Total extent of the contamination problem across the U.S. is not known
- Is the problem localized or ubiquitous
- No federal or state regulations exist, removal treatment technologies are not available
- Are there appropriate analytical methods for perchlorate analysis

PERCHLORATE - ISSUES IN CALIFORNIA

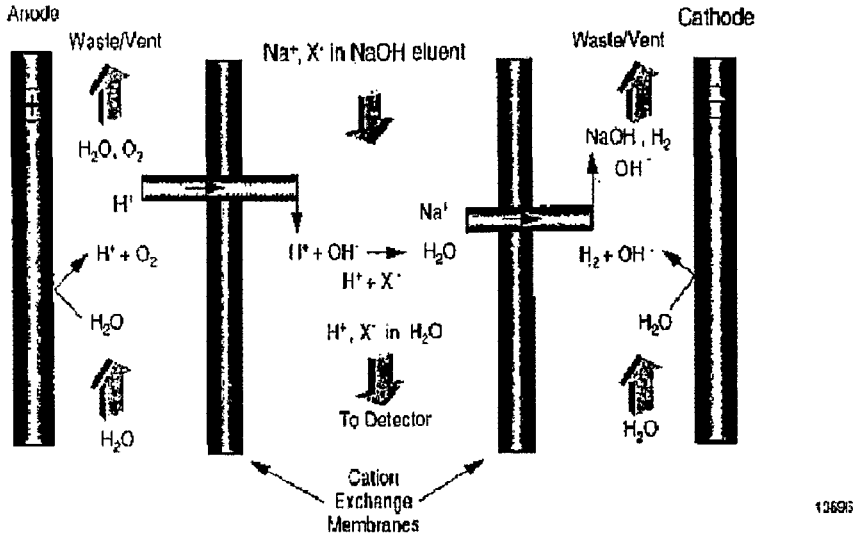
- Perchlorate interferes with thyroid gland function
- U.S. EPA reports adequate health protection corresponding to a range of 4-18 ppb
- Urgent problem in CA, action level of 18 ppb
- >22 groundwater production wells shut down
- California Department of Health Services (CDHS) has developed an ion chromatography (IC) method for the trace analysis of perchlorate



The Role of Chemical Suppression



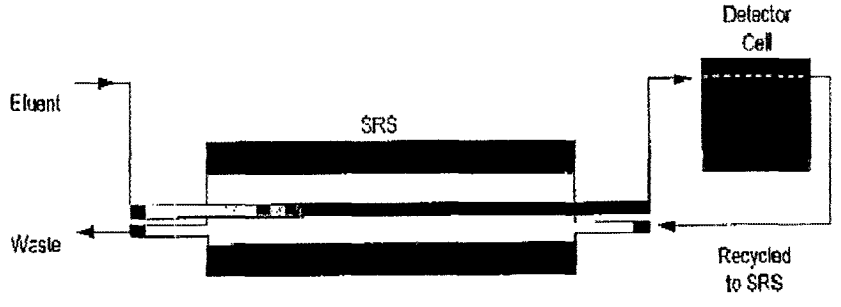
Chemistry and Ion Movement in an Anion SRS®



SRS® Suppression Modes

- Electrolytic regeneration (AutoSuppression®)
  - Eluent recycle
  - External water
- Chemical regeneration
  - Sulfuric acid for ASRS®
  - Tetrabutylammonium hydroxide for CSRS®

SRS™ AutoSuppression™ Mode



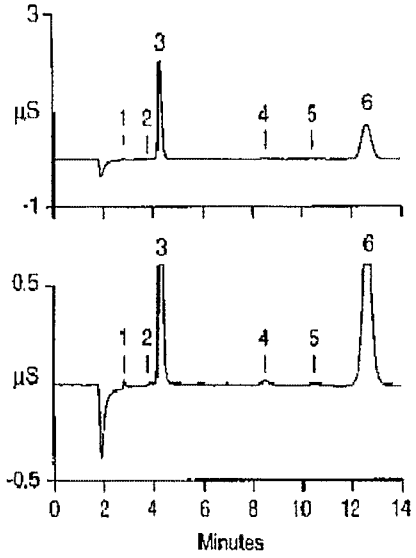
Eluents: ASRS™ — Hydroxide, carbonate/bicarbonate, boric acid/tetraborate

CSRS™ — Methanesulfonic acid (MSA), sulfuric acid

Note: Eluents containing Cl^- or NO_3^- cannot be used in this mode

8416-03

Analysis of Drinking Water on the IonPac® AS14



Column:	IonPac AG14, AS14	
Eluent:	3.5 mM Sodium carbonate 1.0 mM Sodium bicarbonate	
Flow Rate:	1.2 mL/min	
Inj. Volume:	10 µL,	
Detection:	Suppressed conductivity, ASRS™, AutoSuppression™ recycle mode	
Sample:	Drinking water from Milpitas, CA	
Peaks:	1. Fluoride	0.03 mg/L
	2. Bicarbonate	–
	3. Chloride	3.12
	4. Nitrate	0.15
	5. Phosphate	0.04
	6. Sulfate	4.45

12125

United States
Environmental Protection
Agency

Environmental Monitoring
Systems Laboratory
Cincinnati, OH 45268

Office of Research and Development

Revised August 1993

EPA

Method 300.0

Determination of Inorganic Anions by Ion Chromatography

Revision 2.1

John D. Pfaff

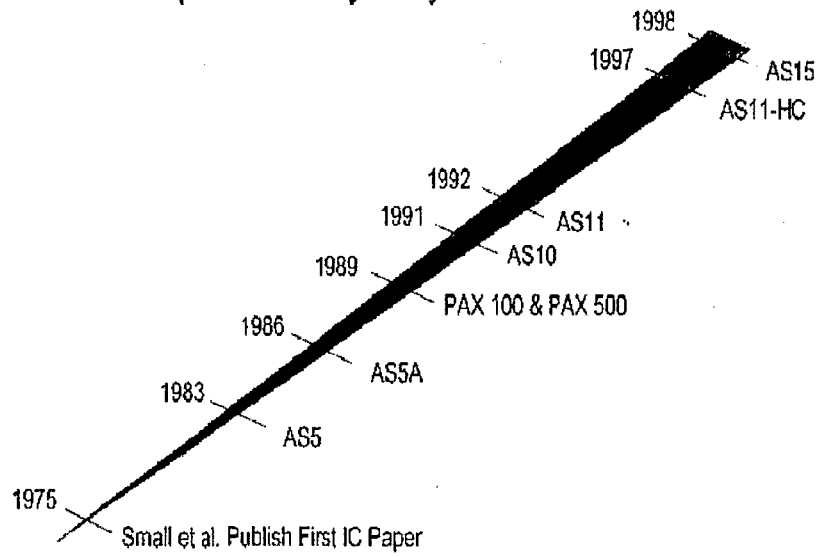
WHAT IS A POLARIZABLE ANION?

- An anion with an "easily" deformable electron cloud
- The anionic form of a "soft" acid
- A "hydrophobic" anion

CHARACTERISTICS OF POLARIZABLE ANIONS

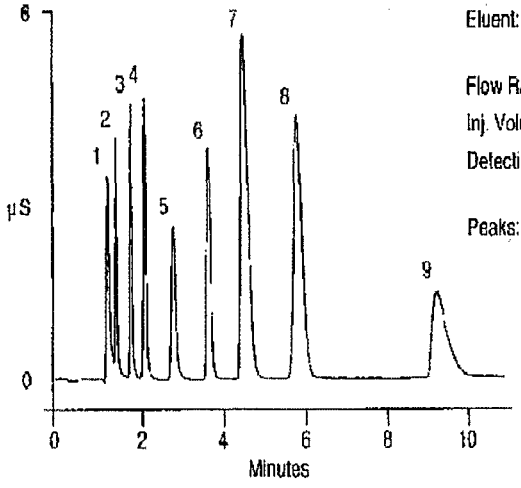
- Low hydration energy
- Small hydrated radius (usually)
- Disruptive of water structure (hydrophobic)
- Strong interactions with π electrons
- High refractive index

Development History of Hydroxide Selective Columns



13274-01

Separation of Polarizable Anions

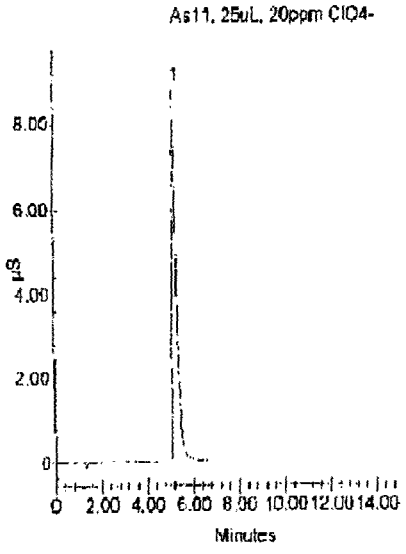


Column:	IonPac® AS11, 4-mm
Eluent:	45 mM Sodium hydroxide in 40% Methanol
Flow Rate:	1 mL/min
Inj. Volume:	25 µL
Detection:	Suppressed conductivity, AutoSuppression external water mode

Peaks:		
	1. Fluoride	2 mg/L
	2. Chloride	2
	3. Nitrate	5
	4. Sulfate	5
	5. Phosphate	10
	6. Iodide	20
	7. Thiocyanate	20
	8. Thiosulfate	20
	9. Perchlorate	20

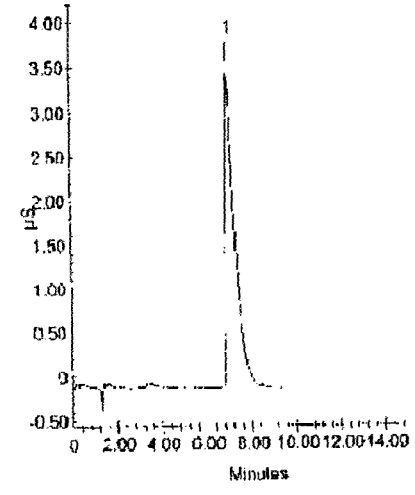
6510-A

Perchlorate on the AS11 Column w/ p-Cyanophenol



Column:	AS11 Column
Eluent:	50 mM Sodium hydroxide 5mM p-Cyanophenol
Flow rate:	1 mL/min
Inj. Volume:	25 µL
Detection:	Suppressed conductivity, ASRS AutoSuppression™ recycle mode
Peaks:	1. ClO_4^- 20 ppm

Perchlorate on the AS11 Column w/o Solvent



Column:	AS11 Column
Eluent:	100 mM Sodium hydroxide
Flow rate:	1 mL/min
Inj. Volume:	25 µL
Detection:	Suppressed conductivity, ASRS AutoSuppression™ recycle mode
Peaks:	1. ClO_4^- 20 ppm

CDHS PERCHLORATE METHOD

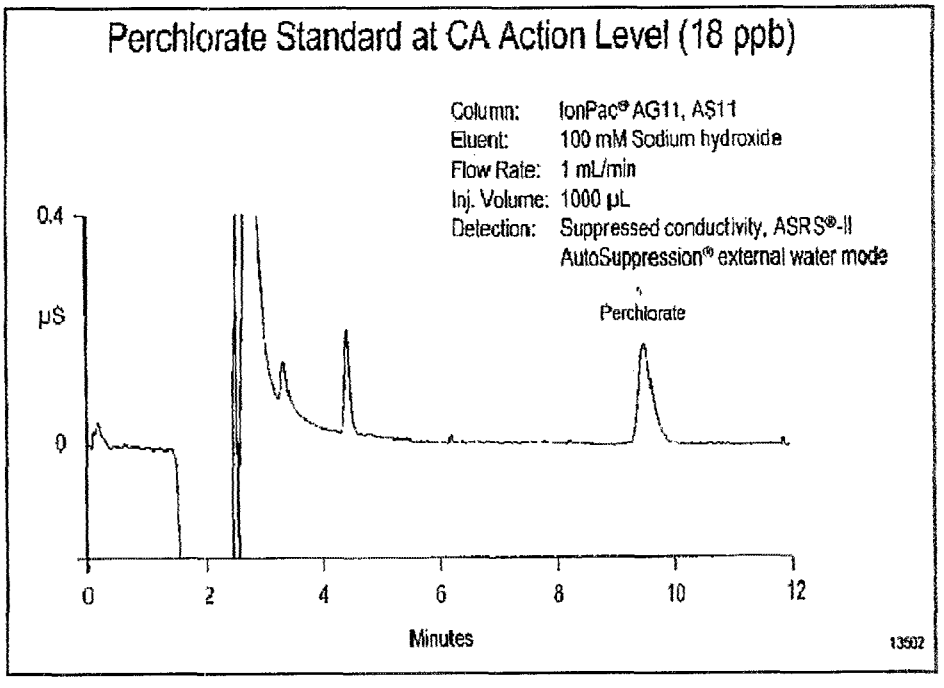
- Large loop (740 uL) injection
- Separation on AS5 anion-exchange column
- Eluent of 120 mM NaOH/2 mM p-cyanophenol
- Suppression using AMMS with 35 mM sulfuric acid regenerant
- Measurement using conductivity detector

CDHS PERCHLORATE METHOD SUMMARY

- MDL in reagent water is 0.7 ug/L (ppb)
- MRL in reagent water is 4.0 ppb
- Linear calibration range of 2 to > 100 ppb
- Recovery of perchlorate spikes at the 1-4 ppb level in the range of 87 - 98%

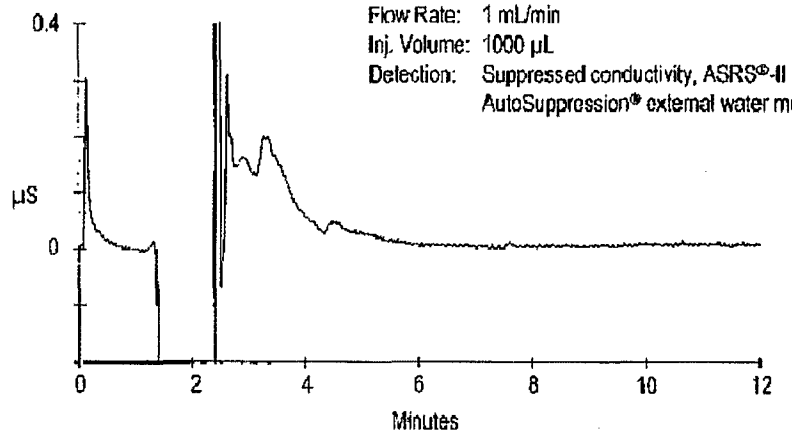
OPTIMIZED DIONEX PERCHLORATE METHOD

- Large loop (1000 uL) injection
- Separation on AS 11 anion-exchange column
- Eluent of 100 mM NaOH (no modifier required)
- Suppression using ASRS with AutoSuppression in external water mode
- Measurement using conductivity detector



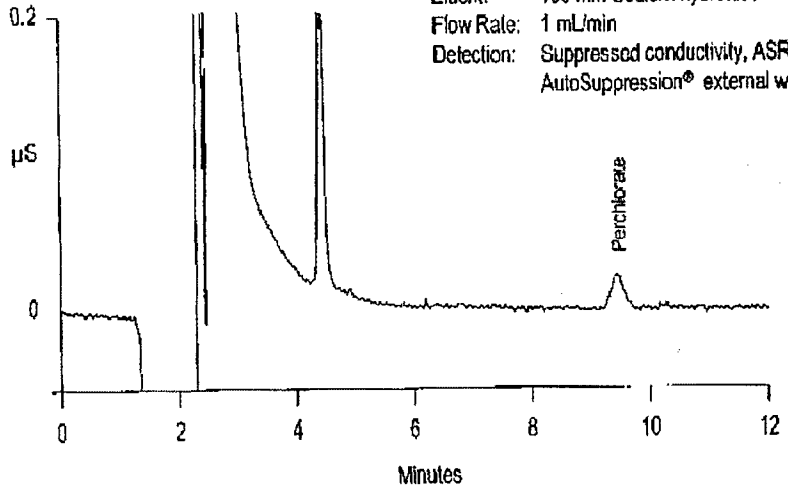
Blank (No Perchlorate) Injection

Column: IonPac® AG11, AS11; DX-120 System
Eluent: 100 mM Sodium hydroxide
Flow Rate: 1 mL/min
Inj. Volume: 1000 µL
Detection: Suppressed conductivity, ASRS®-II AutoSuppression® external water mode



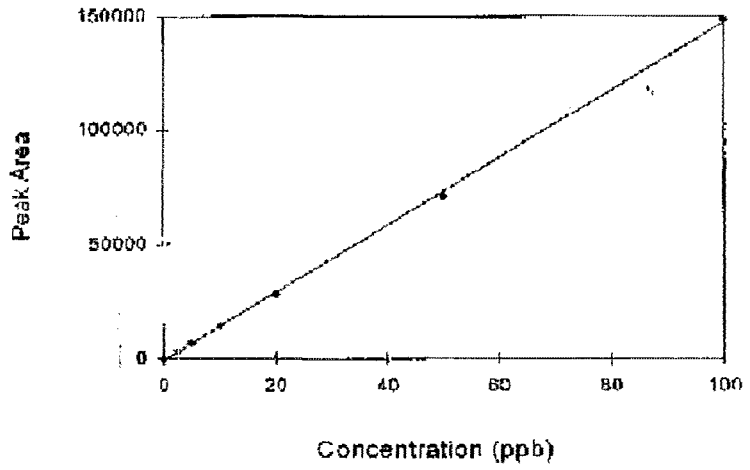
2.5 ppb Perchlorate in Reagent Water

Column: IonPac® AG11, AS11
Eluent: 100 mM Sodium hydroxide
Flow Rate: 1 mL/min
Detection: Suppressed conductivity, ASRS®-II AutoSuppression® external water mode



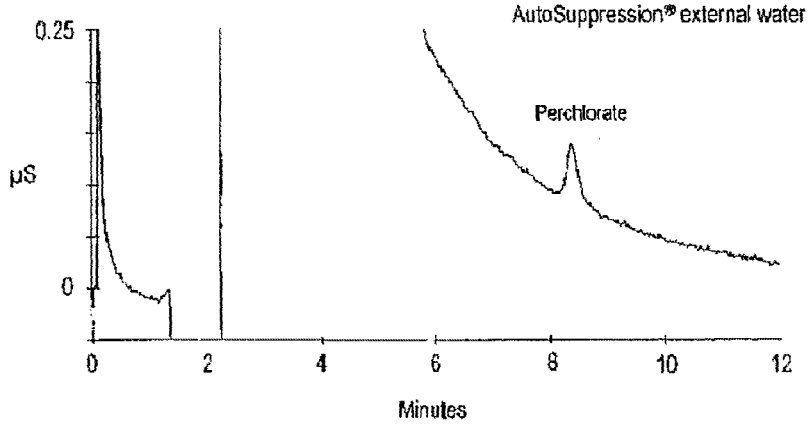
Perchlorate Calibration Curve

2.5 to 100 ppb, $R^2 = 0.9996$



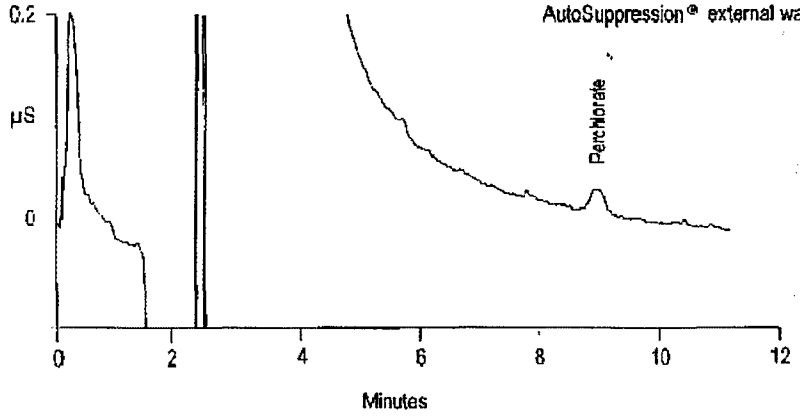
Tap Water Spiked with 4.0 ppb Perchlorate

Column: IonPac® AG11, AS11; DX-120 System
Eluent: 100 mM Sodium hydroxide
Flow Rate: 1 mL/min
Detection: Suppressed conductivity, ASRS®-II AutoSuppression® external water mode



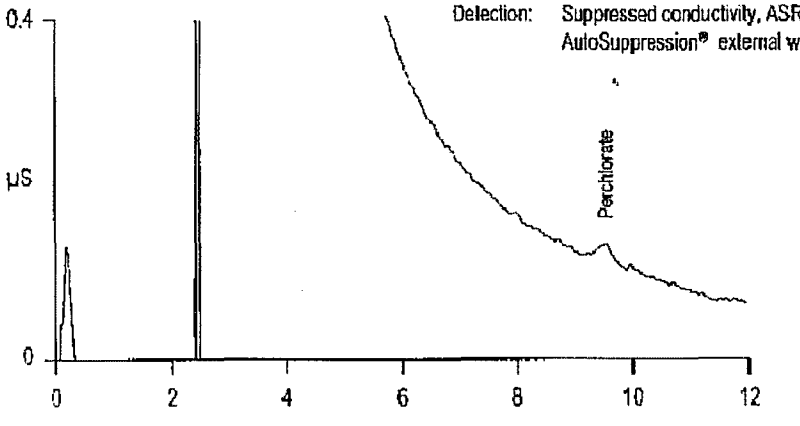
Tap Water Spiked with 2.5 ppb Perchlorate

Column: IonPac® AG11, AS11
Eluent: 100 mM Sodium hydroxide
Flow Rate: 1 mL/min
Detection: Suppressed conductivity, ASRS®-II AutoSuppression® external water mode



2.5 ppb Perchlorate in High (700 ppm) Sulfate

Column: IonPac® AG11, AS11
Eluent: 100 mM Sodium hydroxide
Flow Rate: 1 mL/min
Detection: Suppressed conductivity, ASRS®-II AutoSuppression® external water mode



OPTIMIZED PERCHLORATE METHOD SUMMARY

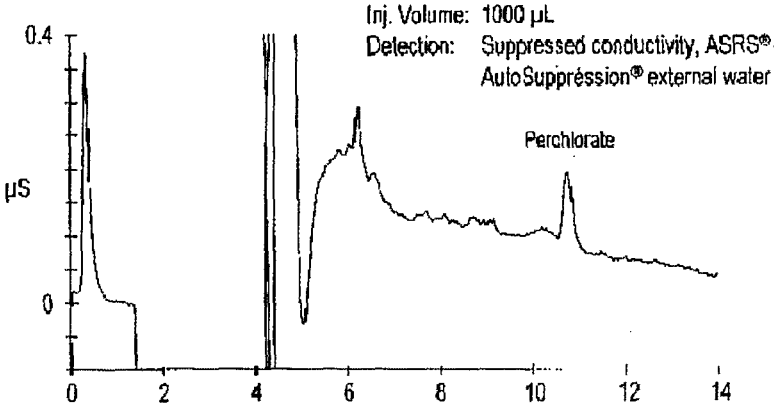
- MDL in reagent water is 0.25 ug/L (ppb)
- MRL in reagent water is ~ 1.0 ppb
- Linear calibration range of 2 to 100 ppb
- Recovery of perchlorate spikes at 2.5 ppb level in the range of 98 - 99%

PERCHLORATE - FURTHER WORK

- Application Laboratory participation in Collaborative Laboratory Study (Col-Lab-I)
- WQTC method presentation
- Use of 2mm AS11 column
- AWWARF project (RFP 2508) collaboration?
- Development of new polarizable anion column
- Application of EG40 to perchlorate analysis

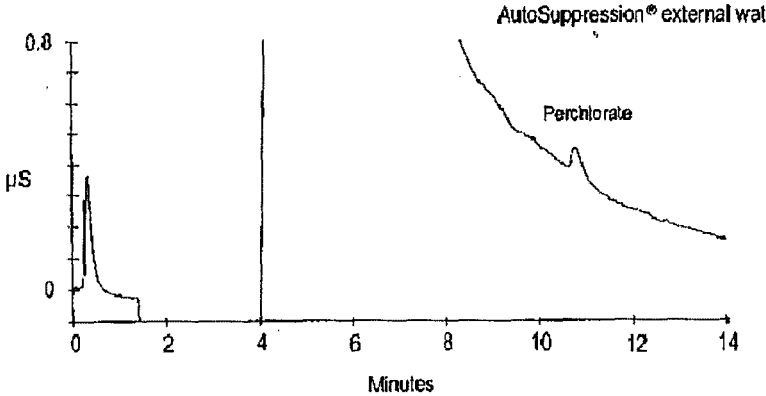
2.5 ppb Perchlorate in Reagent Water, 2mm column

Column: IonPac® AG11, AS11
Eluent: 100 mM Sodium hydroxide
Flow Rate: 0.25 mL/min
Inj. Volume: 1000 µL
Detection: Suppressed conductivity, ASRS®-II
AutoSuppression® external water mode



Tap Water Spiked with 2.5 ppb Perchlorate

Column: IonPac® AG11, AS11 - 2mm
Eluent: 100 mM Sodium hydroxide
Flow Rate: 0.25 mL/min
Detection: Suppressed conductivity, ASRS®-II
AutoSuppression® external water mode



CONCLUSIONS

- Optimized, interference free method for analysis of low ug/L perchlorate in ground and tap water
- Method based on 1000 uL injection, AS11 column, 100 mM NaOH eluent and suppressed conductivity detection using ASRS
- MDL of 0.25 ug/L, MRL of ~ 1.0 ug/L
- Linear calibration range of 2 to 100 ug/L
- Recovery of 98-99% at 2.5 ug/L level

GLOSSARY OF TERMS

- **Ion Chromatography** - Separation-based technique for the analysis of ionic species; typically uses suppressed conductivity detection
- **Eluent** - Ionic solution used to "elute" or push ionic species through analytical (separator) column
- **Analytical Column** - Resin filled tube which separates ionic species (based on ion exchange interactions) into discrete bands prior to detection
- **Suppressor** - Membrane-based device used to reduce eluent conductance and enhance target analyte sensitivity
- **MDL** - Method Detection Limit. Students t-test at the 99% confidence limit applied to 7 replicate injections at ~3x detection limit
- **MRL** - Minimum Reporting Limit. Minimum quantifiable level which may be reported; typically 5x the MDL

Status of Inter-Laboratory Study

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2856 G Street
Wright-Patterson AFB, OH 45433
(P) 937.255.5150 x 3183
(F) 937.255.1474

AS-11 - Users

Air Force Research Lab *

Clayton Laboratories*

Metropolitan Water District of Southern California *

Thiokol *

Orange County Water District*

UDOH - DELS *

Montgomery Watson Labs *

Topics

- Status of Inter-Laboratory Collaborative Study
- Stability Study
  - Container Type and TDS
  - pH
  - Light and Temperature
- Emerging Issues
  - Alternative Methodologies
  - Sample Prep Procedures for Waste Water and Biological Matrices
  - Effects of Organic Solvent on Method Performance
  - Effects of Cations on Method Performance
  - Standard IC Method for Perchlorate Analysis

Method Detection Limit (MDL) - The lowest concentration of a substance which can be measured with 99 percent confidence that the analyte concentration is greater than zero.

Two Ways of Calculating MDL:

■ EPA's Guidelines

MDL = student t-Value x (STDD/M)
Provided that S/N is greater than 3

■ Statistical Calculation

Plot Concentration vs. % CV
MDL is the concentration at 10% CV
Provided that S/N > 3

Practical Quantitation Limit (PQL) – PQL is usually set between 5 to 10 times MDL.

Reporting Limit (RL) – Minimum quantifiable level that may be reported per regulatory purpose. It is Typically set between 5 to 10 times MDL for regulated compounds.

Minimum Reporting Limit (MRL) – Same as RL.

Collaborative-Laboratory Study (Col-Lab1)

- **All-inclusive Policy, however,... Equipment, Analyst, and Method**
- **21 Laboratory Participants**
- **Designed to Study AS-11 and CDHS Methods Performance**
- **Also Incorporates the Following Tasks to Examine Other Analytical Issues**
  - **Task 1.** Methods Validation Study (On-Going)
  - **Task 2.** Holding Time Study
    - **Sub-Task A.** Container Type/TDS (On-Going)
    - **Sub-Task B.** pH (On-Going)
    - **Sub-Task C.** Light, Temperature, Humidity (Complete)
  - **Task 3.** Anion Specific Influence
    - CDHS (Complete)
    - AS-11 Methods (On-Going)

21 Laboratory Participants

Advanced Technology Laboratories

Aerojet

Air Force Research Lab - Environics Lab. *

Air Force Research Lab – Toxicology Laboratory

Alliant Technology Systems

Alpha Analytical

Agricultural Priority Pollutant Laboratory, Inc.

AMPAC

California DHS- Berkley

California DHS-Los Angeles

California Laboratory Services

Clayton Laboratories, Inc. *

Clinical Laboratory of San Bernardino, Inc.

Columbia Analytical Services, Inc.

Dionex Corp. *

E. S. Babcock and Sons, Inc.

LA Agricultural Commission – Environmental Toxicology Lab

Metropolitan Water District of Southern California *

Montgomery Watson Labs *

Thiokol *

Utah Department of Health - Department ELS *

Weck Laboratories, Inc.

* AS-11 users

Task 1. Methods Validation Study

Purpose:

Measure the performance of ion chromatographic methods for the analysis of perchlorate in drinking and groundwater samples. Method performance will be evaluated based on uncertainty (precision) and bias (accuracy)) and measured with respect to perchlorate concentration and total dissolved solids(TDS).

Study Coordinator: Steve Pia

Study Parameters:

Effects of TDS: Three TDS Levels to be determined at the beginning of the study

Concentration Dependence: Four Levels of perchlorate concentration will be verified during the beginning of the study.

Analytical Methods: CDHS and AS-11

Target Groups:

21 Participating Laboratories

QA/QC:

Sample Preparation/Shipping: NERL
TDS measurements: UDOH/DELS or MPWD
pH: UDOH/DELS
EPA 300: APPL, OCWD or UDOH/DELS
Concentration Verification: 3 of 21 Col-Labs
Concentration Determination: 3 of 21 Col-Labs

Milestone(s):

Laboratory Selection: 1 May 98 (On Time)

Sample Prep/Shipment: 8 May 98 (Delayed)

Laboratory Analysis: 8 Jun 98 (Delayed)

Lab Results Due: 8-15 Jun 98 (?)

Draft Report Due: 8 July 98 (?)

Final Peer-Reviewed Report Due: ? Aug 98

Task 2. Holding Time Study
Sub-Task A. Total Dissolve Solids (TDS) and Container Type

Purpose:

Evaluate and assess the stability of perchlorate with respect to TDS and container types. This study will be incorporated into Task 1. Perchlorate concentration determination with respect to container type (glass vs. plastic) and TDS will be measured at fixed interval beyond the initial concentration verification as stated in Task 1.

Study Coordinator: Steve Pia

Study Parameters:

Same as Task 1, except container type is added as a parameter

Effects of TDS: Three TDS Levels
Concentration Dependence: Four Levels
Analytical Methods: CA-DHS and AS-11

Bottle Types: Glass vs. Polyethylene

Target Groups:

Concentration determination conducted by three of the 21 Laboratories on a weekly basis.

QA/QC:

Same as Task 1, except Task 1 effort is now expanded to include concentration verification of perchlorate in both glass and plastic bottles

Sample Preparation/Shipping: NERL
TDS measurements: Measured as part of Task 1
pH: Measured as part of Task 1
EPA 300: APPL, OCWD or UDOH/DELS
Concentration Determination: Beyond the initial concentration verification, 3 of 21 Col-Labs will continue to measure perchlorate concentration in the Col-Lab 1 samples for 3 months on a weekly basis

- **Milestone(s):**

  Laboratory Selection: 1 May 98 (On Time)

  Sample Prep/Shipment: 8 May 98 (Delayed)

  Laboratory Analysis: 8-15 Oct 98 (Delayed)

  Lab Results Due: 8-15 Oct 98 (?)

  Draft Report Due: 8-15 Nov 98 (?)

  Final Peer-Reviewed Report Due: ? Dec 98

Task 2. Holding Time Study
Sub-Task B. pH

Purpose:

Evaluate and assess the stability of perchlorate with respect to pH.

Study Coordinator:

Dr. Sanwat Chaduri, UDOH/DELS

Study Parameters: pH 5.5-8.5

QA/QC:

Concentration Verification: UDOH/DELS

Milestone(s):

TBD

STABILITY AND CONCENTRATION VERIFICATION OF AMMONIUM PERCHLORATE DOSING SOLUTIONS

David T. Tsui, Capt. USAF
AFRL/HEST, BLDG 79
2856 G STREET
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Latha Narayanan
MANTECH GEO-CENTERS JOINT VENTURE
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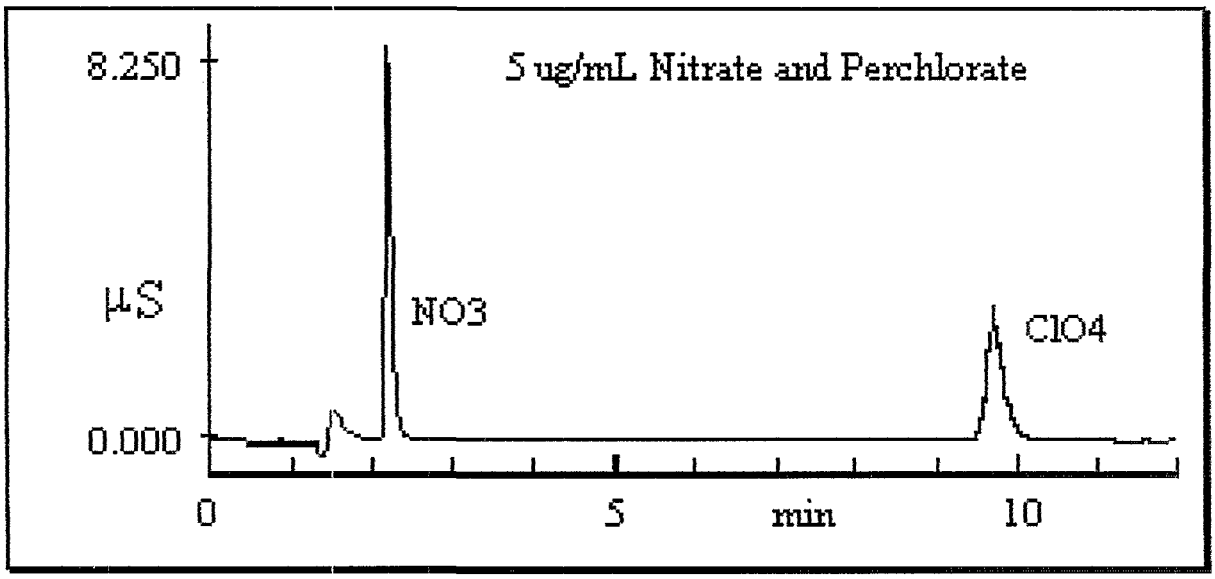
DAYTON OH 45437-0009

David Mattie, Ph.D.
AFRL/HEST, BLDG 79
2856 G STREET
WRIGHT-PATTERSON AFB, OH 45433-7400

- **Methods**
  - **Dionex DX-300, CDM-3, ASRS-II**
  - **AI-350 Autosampler**
  - **AS-11/AG-11 IC/Guard Column, and ATC-1 Anion Trap**
  - **45 mM NaOH in 55/45 H_2O/CH_3OH**
  - **1 mL/min Flow Rate**
  - **50 μL Injection Volume**
  - **10 mL/min Regenerant Flow Rate**
- **Stability Solutions**
  - **50 ppb and 200,000 ppb Stocks Prepared in 4L Polyethylene Carboys**
  - **4 French Clear Square Bottles**
  - **3 French Amber Square Bottles**
  - **Bottles were stored on Animal Cages**

- **Study Conditions**
  - **Temperature: 70 to 72 °F**
  - **Relative Humidity: 60 to 65%**
  - **12/12 Light/Dark Cycle**
  - **Litemate III Model 504 Lite Meter**
  - **Day 7, 15, 36, 50, 61, and 109.**

Method Validation Data



Retention Times:

Nitrate: 2.3 min

Perchlorate: 9.4 min

Peak Width at Half Height:

Nitrate: 0.3 min

Perchlorate: 0.4 min

Perchlorate		Nitrate	
Data Points	**Conc. (µg/mL)**	**Data Points**	**Conc. (µg/mL)**
1	0.050	1	0.048
2	0.050	2	0.051
3	0.052	3	0.051
4	0.054	4	0.051
5	0.050	5	0.052
6	0.050	6	0.048
7	0.050	7	0.049
8	0.049	8	0.050
Avg. Conc. (µg/mL)	0.051	Avg. Conc. (µg/mL)	0.050
Expected Conc. (µg/mL)	0.050	Expected Conc. (µg/mL)	0.050
% Recovery	101%	% Recovery	100%
Standard Deviation	0.002	Standard Deviation	0.002
MDL (µg/mL)	0.005	MDL (µg/mL)	0.005
PQL (10Xmdl)	0.05	PQL (10Xmdl)	0.05

Code of Federal Regulations 40, Chapter 1, Pt. 136, Appendix B

- Calibration Curves: 0.05, 0.1, 0.25, 0.5, 1.0, 2.0, 5.0, 10.0, 25.0, 50.0, 100, 200 ug/mL

(Not Shown, Boringly Linear)

- Linearity: MDL to 40,000 x MDL
- Correlation Variation: 0.9999
- Calibration Curves were Verified by 2nd Source

0.05 μg/mL PERCHLORATE SOLUTION IN CLEAR BOTTLE

	Day 7	Day15	Day36	Day50	Day61	Day109
Bottle A	0.048	0.050	0.051	0.050	0.050	0.050
Bottle B	0.050	0.051	0.048	0.049	0.051	
Bottle C	0.051	0.050	0.048	0.051	0.051	0.050
Bottle D	0.052	0.049	0.050	0.050	0.049	

ANOVA: Single Factor, $\alpha = 0.05$

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Day 7	4	0.201	0.050	2.9E-06		
Day15	4	0.200	0.050	6.7E-07		
Day36	4	0.196	0.049	1.9E-06		
Day50	4	0.201	0.050	5.2E-07		
Day61	4	0.201	0.050	9.2E-07		
Day109	2	0.100	0.050	0		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4.51E-06	5	9.02E-07	0.69858	0.63236	2.85241
Within Groups	2.07E-05	16	1.29E-06			
Total	2.52E-05	21				

An one way analysis of variance (ANOVA) analysis, shown on the bottom of each table, was employed to examine the differences of within group (intra-day) and between groups (inter-day) concentration variations. As shown in Appendix A, three categories of sums of squares (*SS*) are presented in the ANOVA summary report, along with the degrees of freedom (*df*) for the between and within variance. The mean square (*MS*) and the test for homogeneity of variance (*F*-ratio) were calculated from *SS* and *df* by the following equations: $MS = SS/df$ and *F*-ratio = between *MS*/ within *MS*. The *F critical* values at 0.05 rejection level (α) were obtained from Reference 13. As compared to the appropriate F-critical values, the small F-values (test of homogeneity of variance) for all four sets of data indicated that ammonium perchlorate in aqueous solution at 0.05 and 200 μg/mL is stable for 109 days. At a given level, no trend was observed in the perchlorate concentration, as some might expect an increasing trend due to evaporation. Furthermore, no significant perchlorate concentration difference was noted between the solutions stored in amber and clear water bottles at a given concentration. Since the amber bottles are impermeable to light and UV radiation, the results indicated that average 12-hour daily exposure to light does not lead to the degradation of perchlorate in reagent water.

Conclusion:

Ion chromatographic analysis of the stability solutions showed that under controlled room temperature, relative humidity and light intensity, ammonium perchlorate is stable in reagent water for at least 109 days.

Emerging Issues

- Alternative Method(s) for Perchlorate Analysis
  - Triple Sector Quadrupole Mass Spectrometry (TSQ) – Intra-Laboratory Validation
  - Coulometric Detection - Feasibility Study
- Biological Matrices
  - Blood, Urine, and Thyroid
  - Plants, Vegetables, and Fruits
- Environmental Matrices
  - Waste Water
  - Storm Water
- Effects of Organic Solvents on Method Performance
- Effects of Cation(s) on Method Performance

Triple Sector Quadrupole (TSQ) Mass Spectrometry for Perchlorate Analysis

- Instrumentation: Fin. 700 TSQ
- Mobile Phase (MP): 0.5% acetic acid in CAN
- Flow Rate: 75 uL/min
- Injection Volume: 10 uL
- Negative Ion Mode
- Qualitative Identification:
  - Mass Spectra of Perchlorate in MP:
    - 99 and 101 m/z - ClO_4^- and Isotope
    - 140 m/z – $CH_3CN*ClO_4^-$ adduct
    - 159 m/z – $AcOH*ClO_4^-$ adduct
  - Mass Spectra of Other anions
    - Showed no overlapping m/z ratio.
- Quantitation:
  - Selective Ion Monitoring (SIM) of 99 m/z
  - Linear from 1 to 100 ppb
  - Method detection limit: 1 ppb

Emerging Issues

- Alternative Method(s) for Perchlorate Analysis
  - Triple Sector Quadrupole Mass Spectrometry (TSQ)
  - Coulometric
- Biological Matrices
  - Blood, Urine, and Thyroid
  - Plants, Vegetables, and Fruits
- Environmental Matrices
  - Waste Water
  - Storm Water
- Effects of Organic Solvents on Method Performance
- Effects of Cation(s) on Method Performance

Interagency Perchlorate Steering Committee

Edward T. Urbansky
U.S. Environmental Protection Agency
National Risk Management Research Laboratory
Water Supply and Water Resources Division
Cincinnati, Ohio 45268

1

Treatment Technologies for Perchlorate Reduction

2

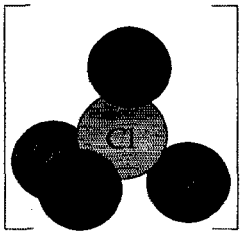
Treatment Technologies for Perchlorate Reduction

There is no one technique that will work for every case.

There is no standard or benchmark for evaluating performance.

3

Treatment Technologies for Perchlorate Reduction



1–

- An oxyanion of chlorine
- A strong oxidizing agent (thermodynamics)
- A very sluggish species (kinetics)

4

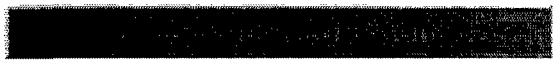
Treatment Technologies for Perchlorate Reduction

Name	Oxidation State	Formula
Perchlorate	+7	ClO_4^-
Chlorate	+5	ClO_3^-
Chlorite	+3	ClO_2^-
Hypochlorite	+1	ClO^-
Dichlorine	0	Cl_2
Chloride	−1	Cl^-

Increasing oxidizing strength ↑

5

Treatment Technologies for Perchlorate Reduction



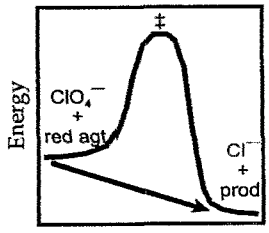
$$\overset{+7}{ClO_4^-} + 8\,e^- + 8\,H^+ \rightarrow \overset{-1}{Cl^-} + 4\,H_2O$$

$E° = 1.287$ volts

A reducing agent transfers electrons to the chlorine atom in a perchlorate ion, converting it to chloride.

6

Treatment Technologies for Perchlorate Reduction



In general, perchlorate reduction is very slow even though perchlorate is a strong oxidizing agent.

Common reductants (e.g., thiosulfate, sulfite) show no measurable reaction.

7

Treatment Technologies for Perchlorate Reduction

A number of air-sensitive metal species can reduce perchlorate, but they cannot be used directly in water treatment because they are still too slow and their products would have to be removed.

Titanium(III)	Methylrhenium dioxide, CH_3ReO_2
Vanadium(II, III)	Dimolybdenum(III), Mo_2^{6+}
Chromium(II)	Molybdenum(III)
Ruthenium(II)	

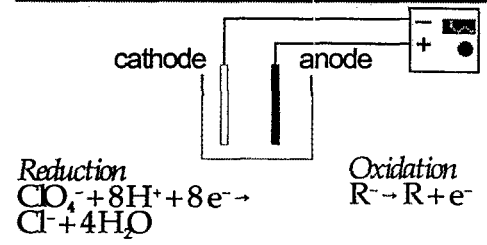
8

Treatment Technologies for Perchlorate Reduction

- Expense of materials
- Slowness of reaction
- Toxicity of by-products
- Removal of by-products

9

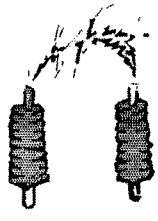
Treatment Technologies for Perchlorate Reduction



10

Treatment Technologies for Perchlorate Reduction

- Tungsten carbide
- Ruthenium
- Platinum
- Aluminum
- Titanium
- Aluminum oxide
- Carbon (doped with Al_2O_3 or Cr_2O_3)



11

Treatment Technologies for Perchlorate Reduction

- Advantages
  - Nontoxic by-products
  - Well-known technique
- Disadvantages
  - Construction/implementation expense
  - Operation expense (electricity)
  - Electrolysis of water
  - Slowness (reaction and diffusion)
  - Safety (high voltage)

12

Treatment Technologies for Perchlorate Reduction

The use of biological organisms, especially bacteria, to chemically reduce perchlorate to other chemical species

Perchlorate-reducing bacteria

Ideonella dechloratans
Proteobacteria
Vibrio dechloraticans Cuzensove B-1168
Wolinella succinogenes HAP-1

13

Treatment Technologies for Perchlorate Reduction

USAF, Tyndall AFB, Florida

The bacterium *Wolinella succinogenes* is capable of using perchlorate as an oxidizing agent (electron acceptor) for metabolism.

The USAF and AF Research Labs have developed a bioreactor for this purpose.

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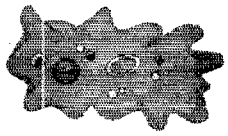
Treatment Technologies for Perchlorate Reduction

- Advantages
  - Nontoxic by-products
  - Versatility
  - Speed
- Disadvantages
  - Acceptance
  - Regulatory barriers
  - Construction/implementation costs
  - Hardiness of bacteria



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Treatment Technologies for Perchlorate Reduction

- Bacteria use a biological catalyst or enzyme, called a *reductase*, to reduce perchlorate.
- It may be possible to purify this enzyme and use it directly as a reactant for chemical reduction (addition or tethering).
- Perchlorate reductases evolved from nitrate reductases used by nitrogen-fixing bacteria (e.g., those in legumes).

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Treatment Technologies for Perchlorate Reduction

- Advantages
  - No toxic perchlorate by-products
  - Fast reaction time
  - High effectiveness
- Disadvantages
  - High expense in producing enzyme
  - High maintenance
  - Difficult implementation
  - Enzyme by-products unstudied

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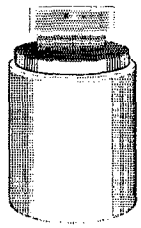
Treatment Technologies for Perchlorate Reduction

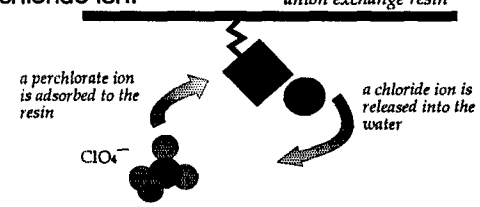


- Anion exchange
- Membrane processes
  - Nanofiltration
  - Reverse osmosis
  - Electrodialysis

18

Treatment Technologies for Perchlorate Reduction

A positively charged resin is used to exchange the perchlorate ion for a harmless chloride ion.



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Treatment Technologies for Perchlorate Reduction

Oak Ridge National Laboratory
Oak Ridge, Tennessee

Selective pertechnetate (TcO_4^-) removal to parts per trillion ($pg\ mL^{-1}$) levels

20

Treatment Technologies for Perchlorate Reduction

Anion exchange is used to remove nitrate from water. NO_3^-

- Nitrate-selective resins already exist.
- Perchlorate and nitrate have similar physical properties (charge, size, aquation).
- Therefore, these resins are expected to be effective in removing perchlorate.
- However, permissible nitrate concentrations are much higher than the perchlorate action level.

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Treatment Technologies for Perchlorate Reduction

Ion Exchange

- Advantages
  - Reasonable operating costs
  - Well-developed technique
  - Easy implementation
  - Effectiveness
- Disadvantages
  - Waste disposal from regeneration
  - Moderate selectivity
    - Distribution system effects
    - Resin lifetime

22

Treatment Technologies for Perchlorate Reduction

Reverse Osmosis

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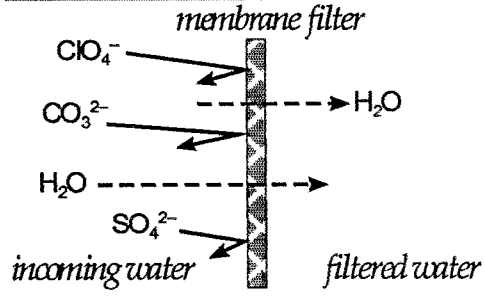
Treatment Technologies for Perchlorate Reduction

Reverse Osmosis



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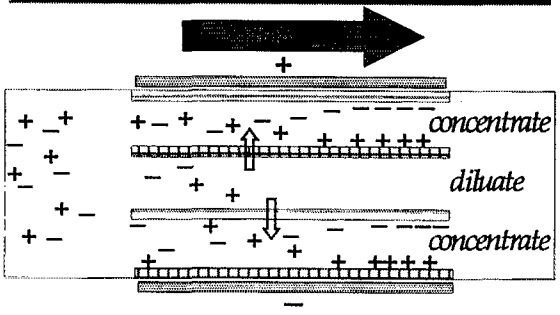
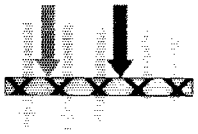
Treatment Technologies for Perchlorate Reduction



25

Treatment Technologies for Perchlorate Reduction

- Advantages
  - High effectiveness
  - Low operating cost
  - High throughput
  - Easy implementation
- Disadvantages
  - Low selectivity
    - Distribution system effects
    - Palatability
  - Waste effluent disposal



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Treatment Technologies for Perchlorate Reduction

- Reverse Osmosis and Nanofiltration
- Ozone/GAC (Chemical Reduction?)
- Biological Reduction
- Anion Exchange

27

Treatment Technologies for Perchlorate Reduction

- Incomplete health effects studies
- Success at reaching trace concentrations
- Distribution system effects

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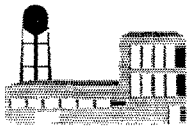
Treatment Technologies for Perchlorate Reduction



- Effects on other treatment processes
- Effects from other treatment processes
- Reliability

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Treatment Technologies for Perchlorate Reduction

- Palatability
- Time
- Expense

30

Treatment Technologies for Perchlorate Reduction

The best solution for a specific situation is likely to be a combination of technologies.

- Anion exchange + bioremediation
- Nanofiltration + blending

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Treatment Technologies for Perchlorate Reduction

Small systems may benefit from a number of techniques that will not work in large systems.

- Reverse osmosis
- Anion exchange

32

Treatment Technologies for Perchlorate Reduction

- Some techniques lend themselves to point-of-use devices.
- Both anion exchange and RO may be used at individual sites or for very small systems.
- No standards presently exist for purification systems; however, that could be rectified fairly quickly.

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Treatment Technologies for Perchlorate Reduction

Congress has appropriated $2 million to the East Valley Water District for studies on perchlorate.

The American Water Works Association Research Foundation has requested proposals.

EPA anticipates an initiative in fiscal year 2000.

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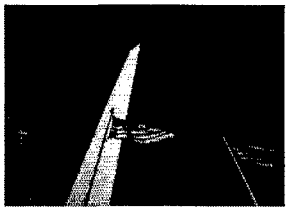
Treatment Technologies for Perchlorate Reduction

- Perchlorate is unlike other contaminants already regulated.
- Effective management will require long and short term responses.
- The best solutions will only come about through continued cooperation among state, local, and federal agencies.



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Treatment Technologies for Perchlorate Reduction

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Ammonium Perchlorate Treatment Technology Development

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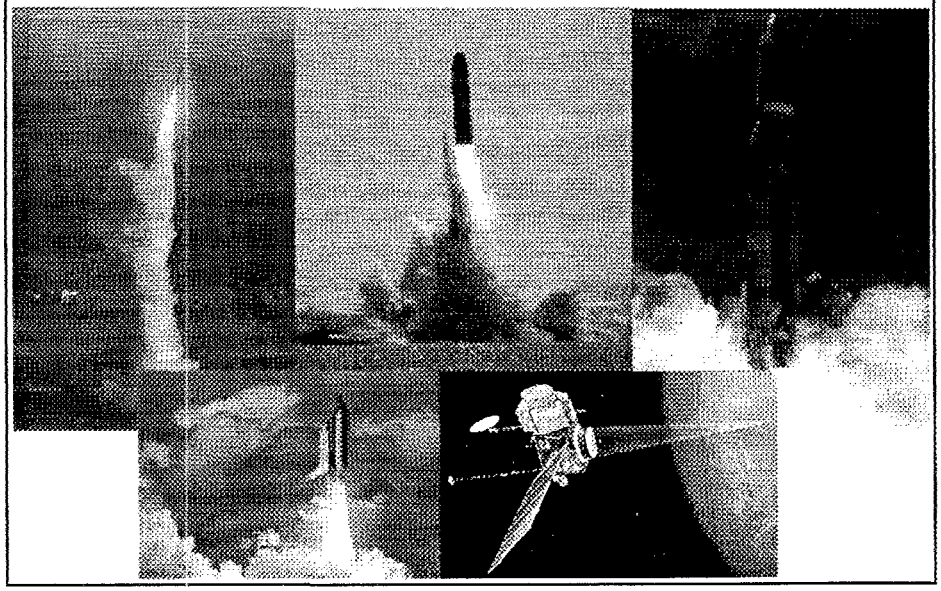
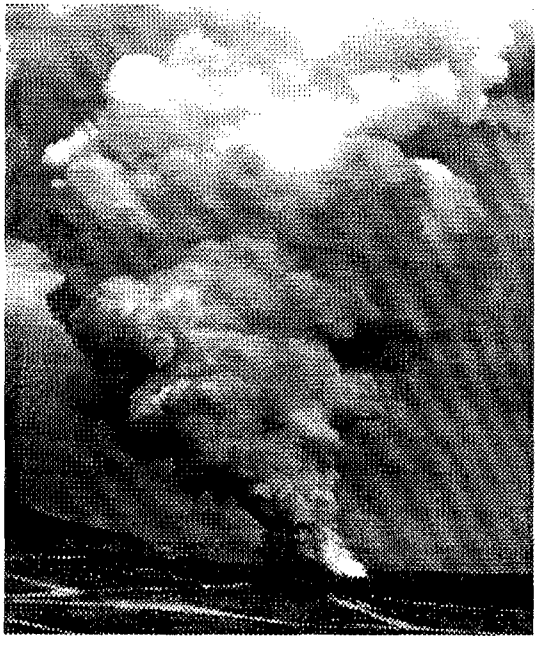
Ammonium Perchlorate - A National Technical Asset
Integral to Strategic Defense Systems - ICBM, SLBM, NRO



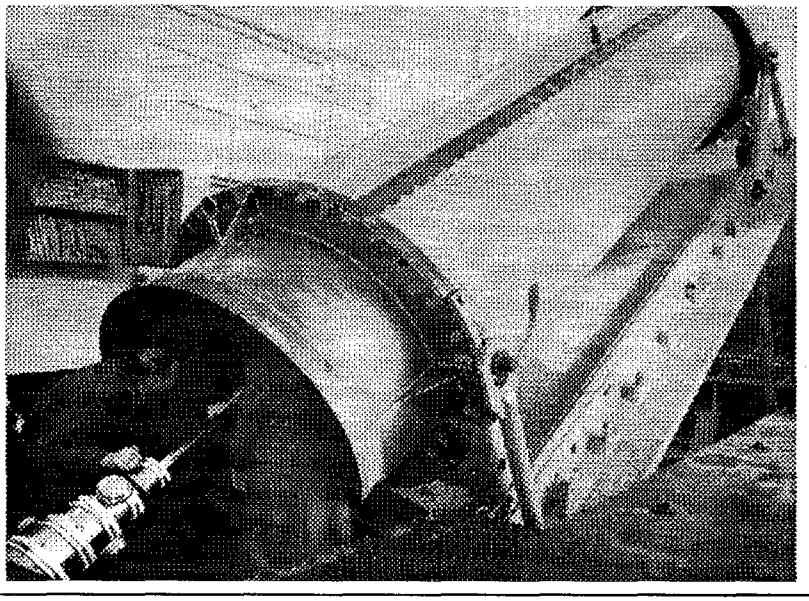


Peace Keeper 1st Stage (98,000 lb)

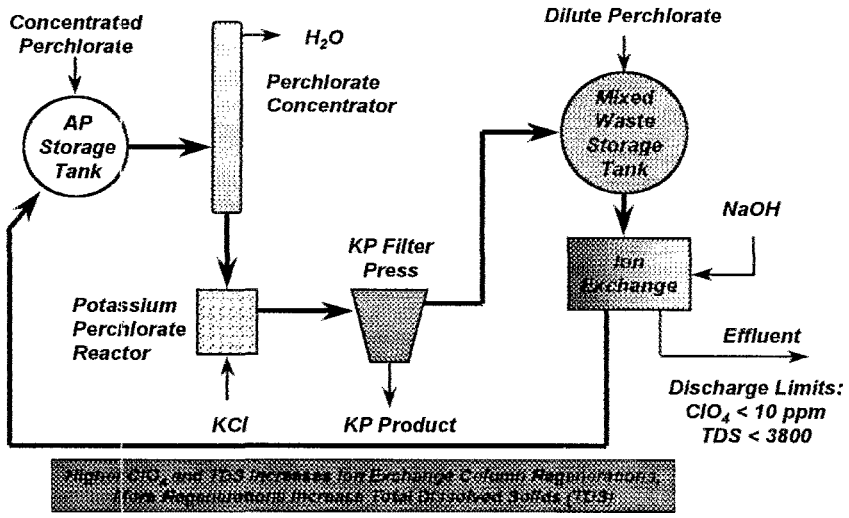
Requirement

- ***Increased Demand for Open-Burn/ Open-Detonation (OB/OD) Facilities with Large-Rocket Motor Capacity.***
  - ***START II***
  - ***Nunn-Luger***
  - ***Non-Proliferation Treaty***
  - ***Multi-National Force Reduction Treaty***
- ***Decreased Availability of OB/OD Facilities.***
  - ***Clean Air Act Amendment - 1990 (CAAA)***
  - ***Base Realignment and Closure (BRAC)***
- ***Statement of Operational Need (SON 003-90)***
  - ***Joint Logistics Commanders***
  - ***Gen McDonald- AFLC/CC***

High-Pressure Water Washout of Solid Propellant

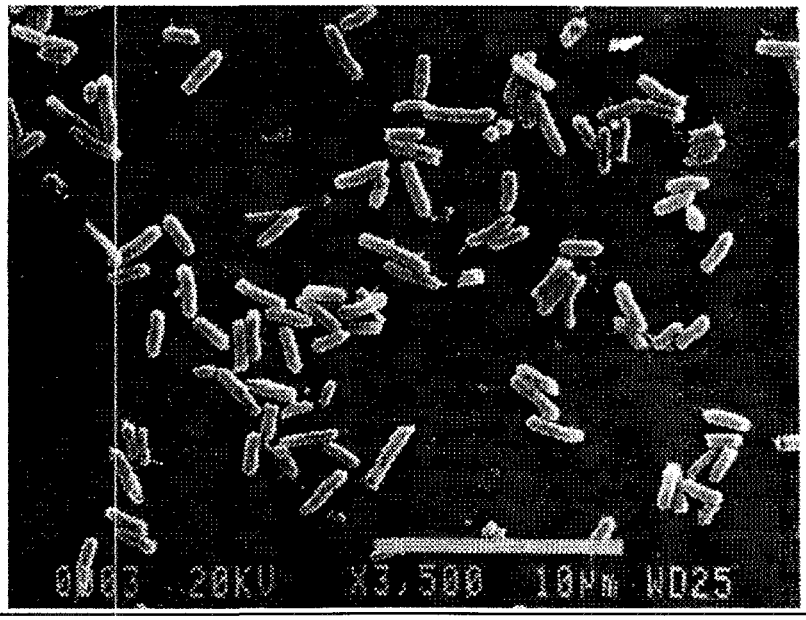


Perchlorate Recovery Process

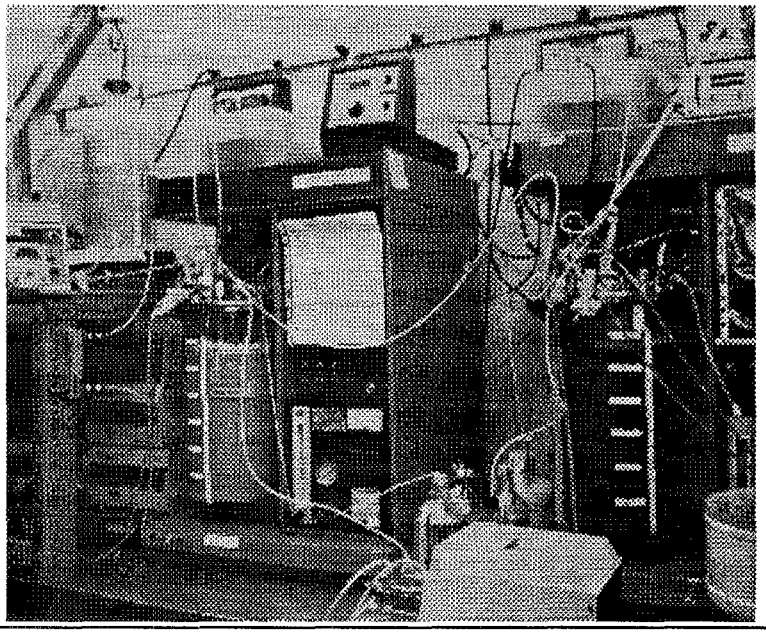


Higher ClO_4 and TDS Increases Ion Exchange Column Regenerations, More Regenerations Increase Total Dissolved Solids (TDS)

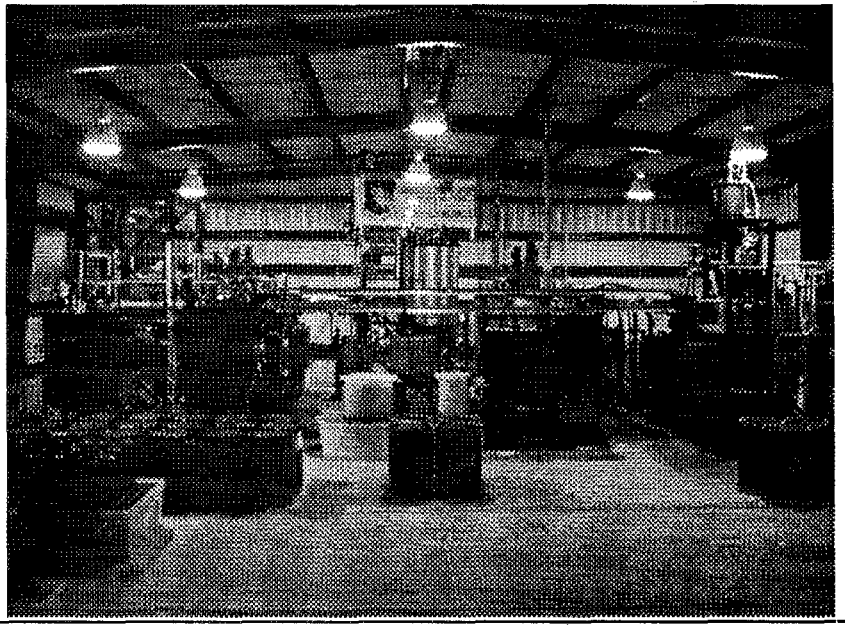
Wolinella succinogenes HAP-1



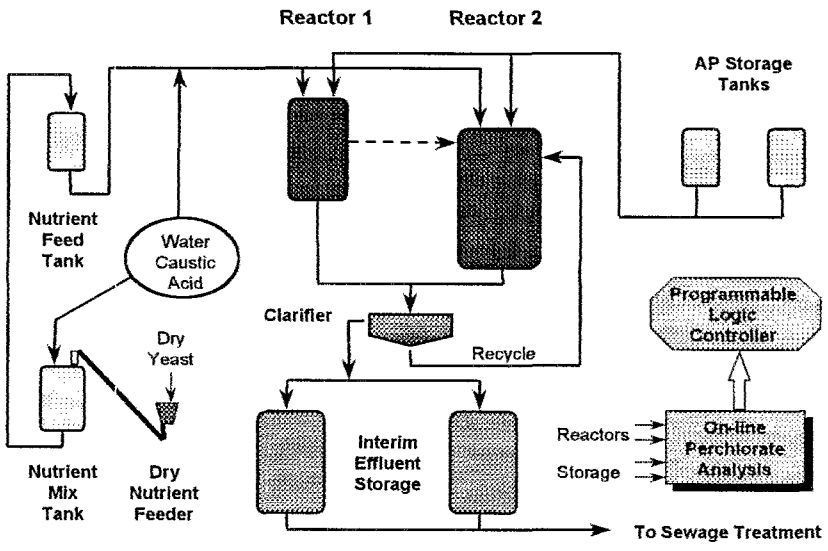
Bench-Scale Reactor System



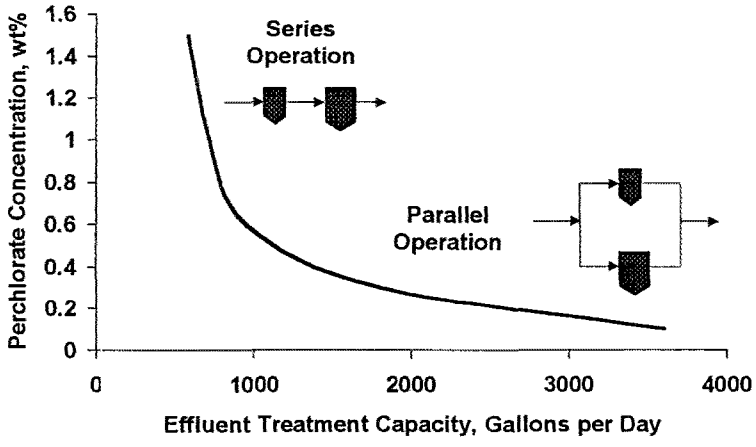
Production-Scale AP Reactor System

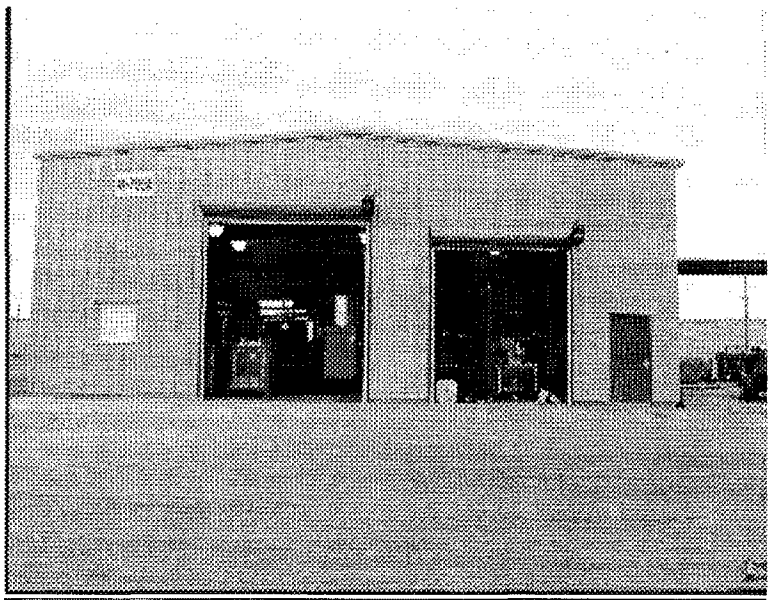


Ammonium Perchlorate Biodegradation Process

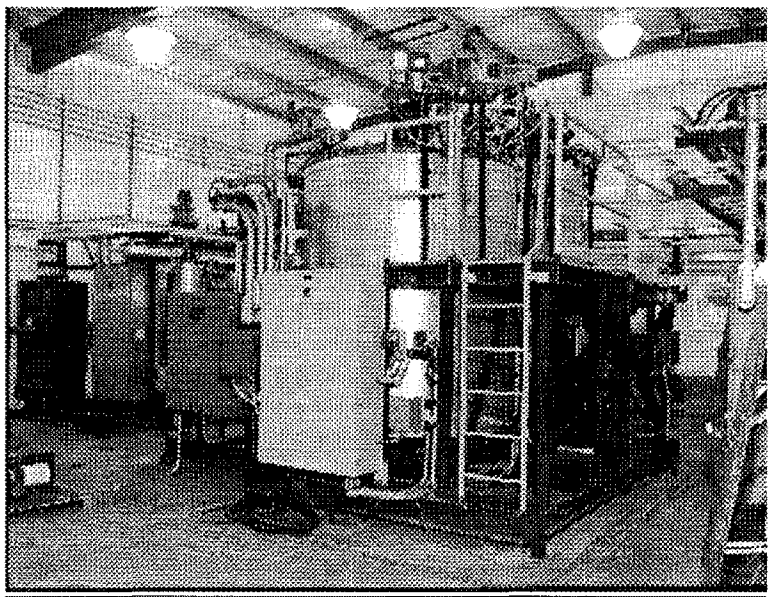


Effect of Perchlorate Concentration on Capacity



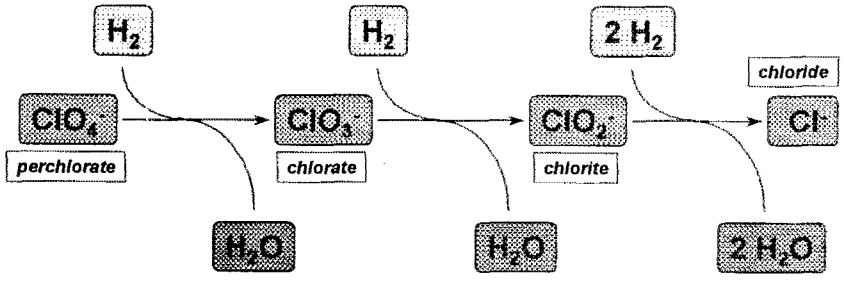


Building at Thiokol Housing the Ammonium Perchlorate Bioreactor System

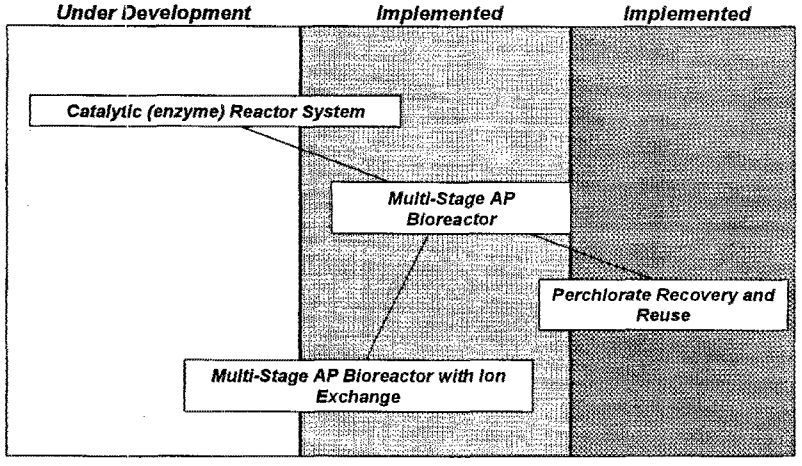


Primary and Secondary Ammonium Perchlorate Reactors

Metabolic Pathway for Energy Production in *Wolinella succinogenes* HAP1



AP Treatment Technology vs Process Requirement



10 ppb - 10,000 ppb	10 - 10,000 ppm	1-20 wt. %
Drinking Water, Ground Water	Production Waste Water	Bulk Propellant
Low Concentration	Moderate Concentration	High Concentration

Perchlorate Concentration [ClO_4^-]

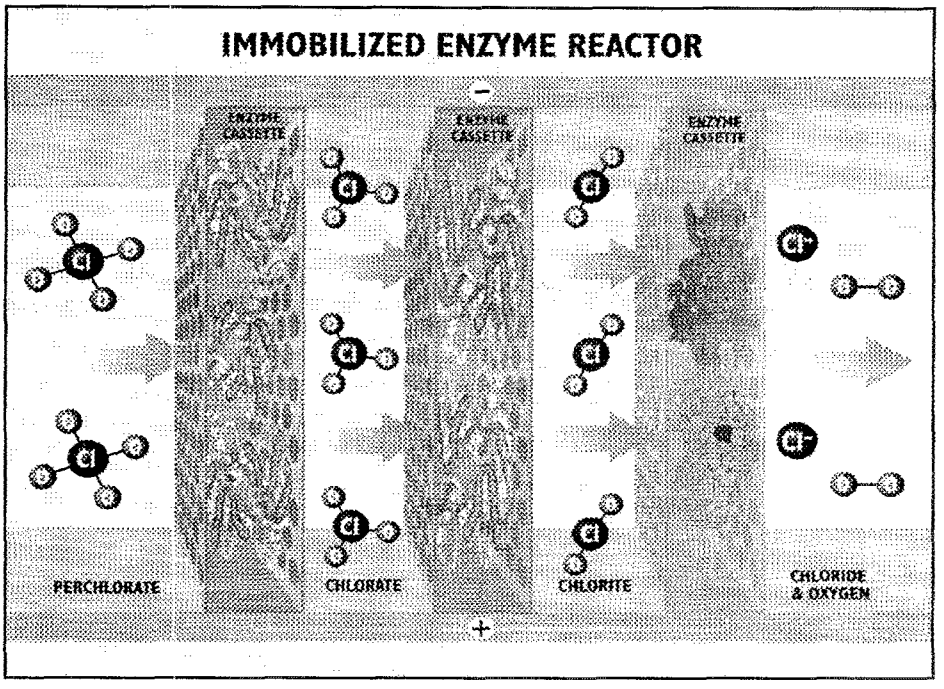
Low-Concentration AP, High-Volume Wastewater Treatment

Two Approaches

1. *New (or Improved) Unit Operations Enabling Utilization of Demonstrated Moderate-Concentration AP Water Treatment*
   - *Reverse Osmosis*
     - *Limited Capacity*
     - *Requires Effluent Reconditioning*
   - *Capacitive Deionization*
     - *Small Electrochemical Driving Force Limits Capacity*
     - *Requires Effluent Reconditioning*
   - *Ion Exchange*
     - *Resin Regeneration Very Difficult*
     - *Efficacy Uncertain at ppb Concentration Level*
     - *Selectivity Difficult*
     - *May Require Effluent Reconditioning*

Low-Concentration AP, High-Volume Wastewater Treatment (cont.)

2. *New Process for Treating Low-Concentration AP Water Directly*
   - *Conventional Catalytic Reactor System*
     - *Non-Selective*
     - *Mass-Transfer Limited*
     - *Unknown Kinetics, Unknown Efficacy*
   - *Enzyme Catalytic Reactor System*
     - *Anion Specific Selectivity*
     - *High Capacity*
     - *Wide Application Range*
     - *Affect of Other Contaminants Unknown*
     - *Requires Multi-Disciplinary Effort*
     - *System Sustainability Uncertain*



Air Force Benefit

- ***The payoff to the Air Force from this continued effort is reduction of weapon system operational cost as well as ensured continued sustainability.***
- ***Manufacturing and maintenance facilities are under ever increasing constraints regarding the life-cycle management of materials used in weapon systems and their manufacture.***
- ***Technology insertion opportunities are made possible by the continued participation of MLQ in Air Force unique materials selection, development, and management through the weapon system life-cycle.***

Points-of-Contact

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Biological Treatment of Perchlorate at Low Concentrations in Water

Baldwin Park Operable Unit San Gabriel Basin

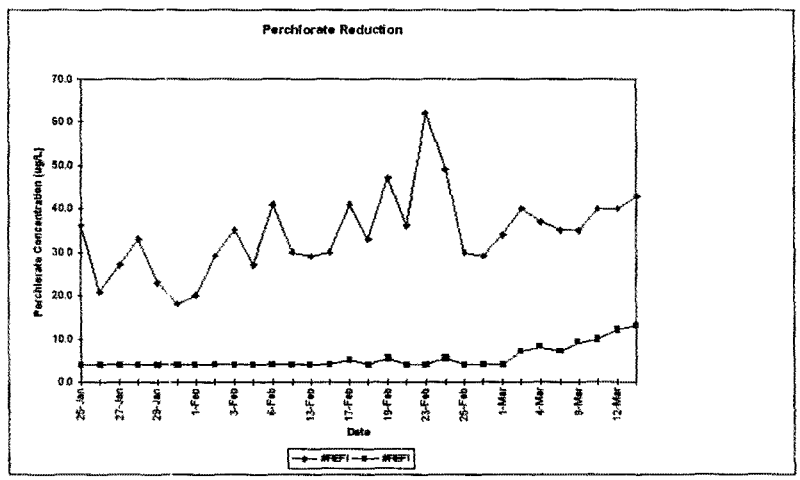
John G. Catts Ph.D.
Harding Lawson Associates

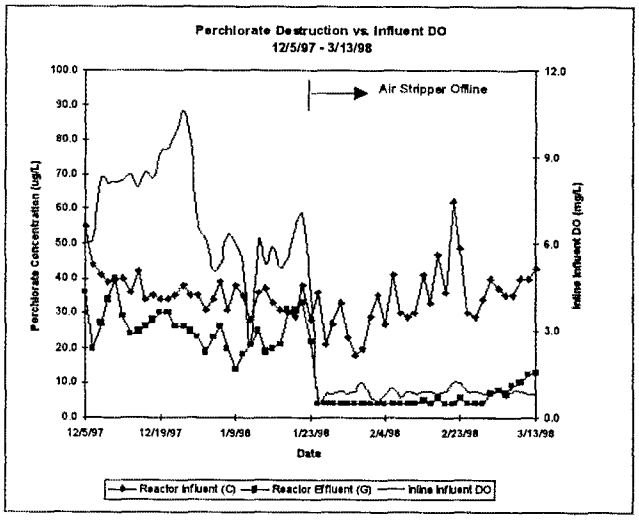
Treatability Study Objectives

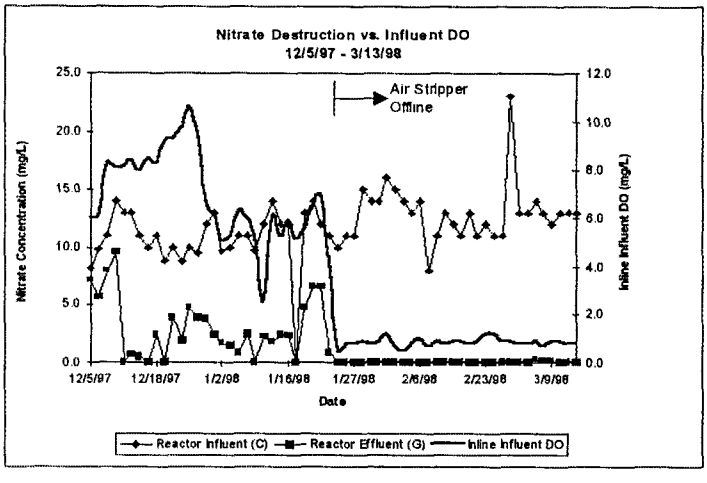
- Treat water containing 50 to 100 ug/L perchlorate
- Treat water containing 4 to 6 mg/L nitrate
- Produce effluent with perchlorate of 18 ug/L or lower
- Test alternate source of microorganisms
- Assess potability of effluent

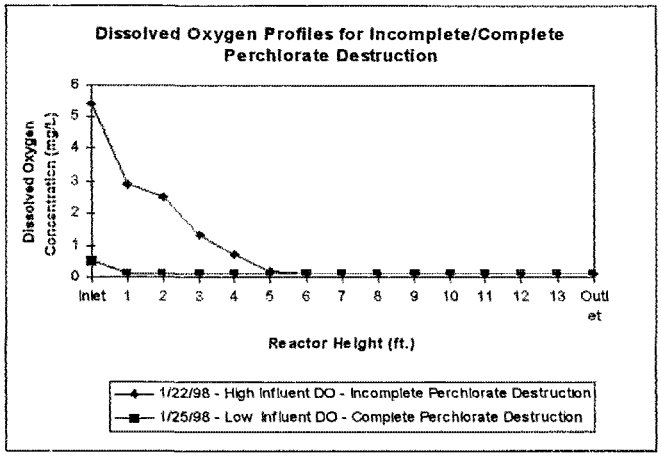
Treatment Technology

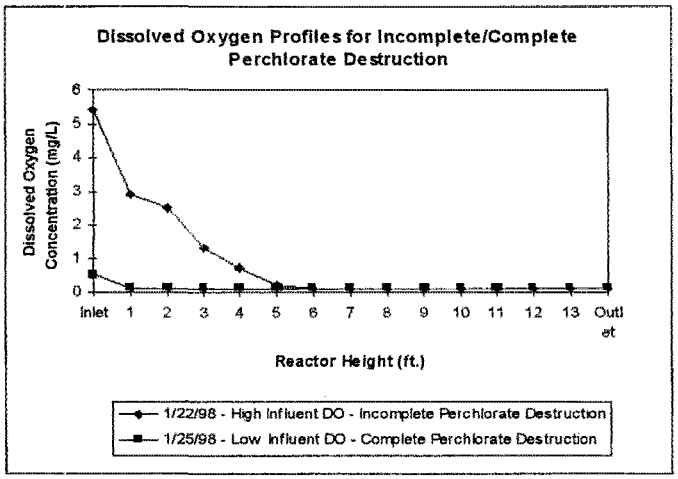
- Attached-growth fluidized bed bioreactor
- Granular activated carbon
- Recycle capacity
- Carbon separation
- Feed system for nutrients (N and P)
- Feed system for organic substrate (ethanol)

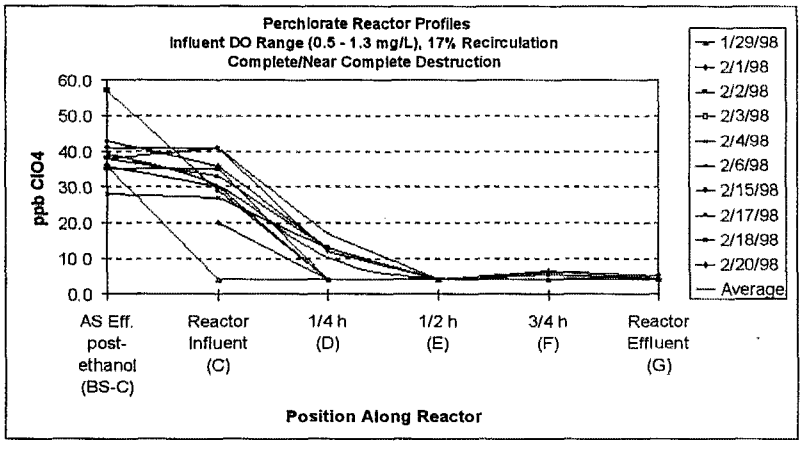


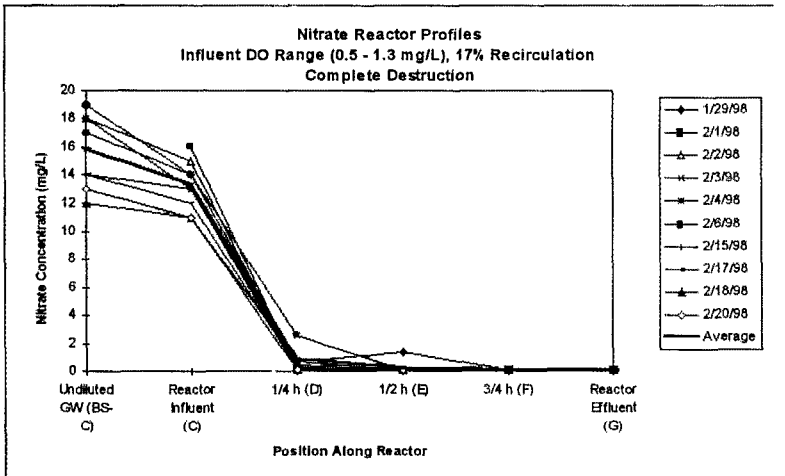

Perchlorate Destruction vs. Influent DO
12/5/97 - 3/13/98
Air Stripper Offline
Perchlorate Concentration (ug/L)
Inline Influent DO (mg/L)
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
12.0
9.0
6.0
3.0
0.0
12/5/97
12/19/97
1/9/98
1/23/98
2/4/98
2/23/98
3/13/98
Date
Reactor Influent (C)
Reactor Effluent (G)
Inline Influent DO

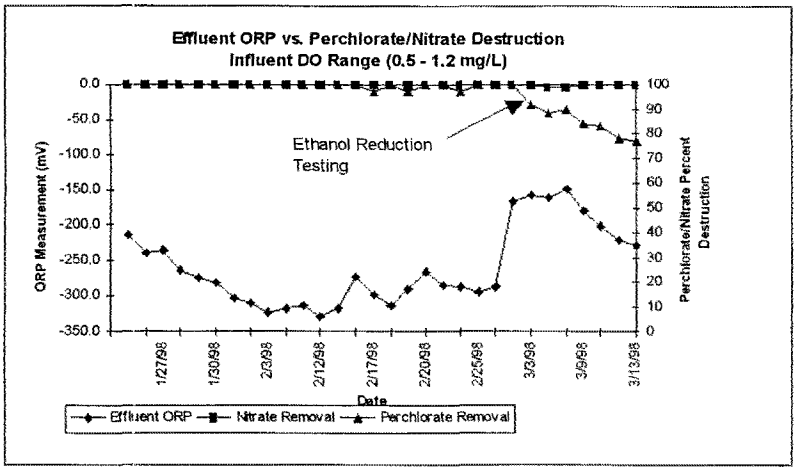

Nitrate Destruction vs. Influent DO
12/5/97 - 3/13/98
Air Stripper Offline
Nitrate Concentration (mg/L)
Inline Influent DO (mg/L)
25.0
20.0
15.0
10.0
5.0
0.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
12/5/97
12/18/97
1/2/98
1/16/98
1/27/98
2/6/98
2/23/98
3/9/98
Date
Reactor Influent (C)
Reactor Effluent (G)
Inline Influent DO

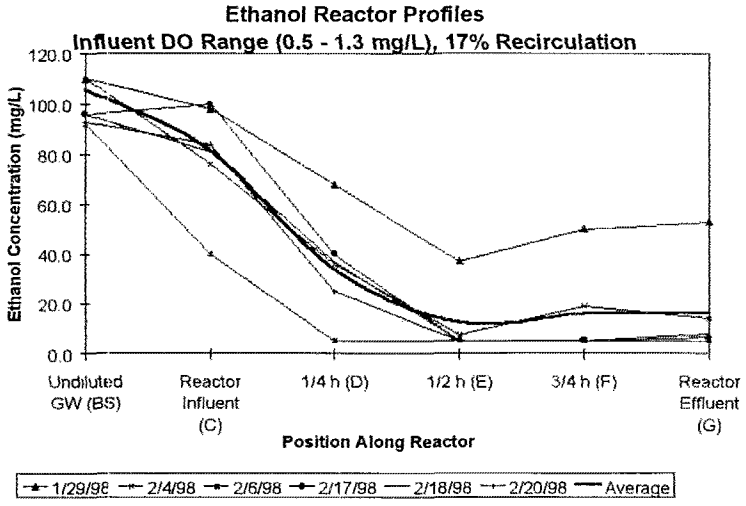

Dissolved Oxygen Profiles for Incomplete/Complete Perchlorate Destruction
Dissolved Oxygen Concentration (mg/L)
0
1
2
3
4
5
6
Inlet
1
2
3
4
5
6
7
8
9
10
11
12
13
Outlet
Reactor Height (ft.)
1/22/98 - High Influent DO - Incomplete Perchlorate Destruction
1/25/98 - Low Influent DO - Complete Perchlorate Destruction

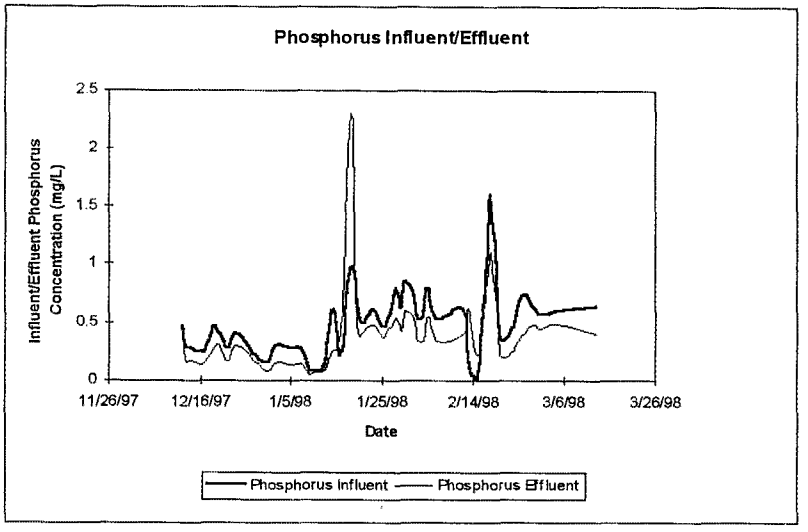

Dissolved Oxygen Profiles for Incomplete/Complete Perchlorate Destruction
Dissolved Oxygen Concentration (mg/L)
0
1
2
3
4
5
6
Inlet
1
2
3
4
5
6
7
8
9
10
11
12
13
Outlet
Reactor Height (ft.)
1/22/98 - High Influent DO - Incomplete Perchlorate Destruction
1/25/98 - Low Influent DO - Complete Perchlorate Destruction


Perchlorate Reactor Profiles
Influent DO Range (0.5 - 1.3 mg/L), 17% Recirculation
Complete/Near Complete Destruction
ppb ClO4
60.0
50.0
40.0
30.0
20.0
10.0
0.0
AS Eff. post-ethanol (BS-C)
Reactor Influent (C)
1/4 h (D)
1/2 h (E)
3/4 h (F)
Reactor Effluent (G)
Position Along Reactor
1/29/98
2/1/98
2/2/98
2/3/98
2/4/98
2/6/98
2/15/98
2/17/98
2/18/98
2/20/98
Average


Nitrate Reactor Profiles
Influent DO Range (0.5 - 1.3 mg/L), 17% Recirculation
Complete Destruction
Nitrate Concentration (mg/L)
20
18
16
14
12
10
8
6
4
2
0
Undiluted GW (BS-C)
Reactor Influent (C)
1/4 h (D)
1/2 h (E)
3/4 h (F)
Reactor Effluent (G)
Position Along Reactor
1/29/98
2/1/98
2/2/98
2/3/98
2/4/98
2/6/98
2/15/98
2/17/98
2/18/98
2/20/98
Average


Effluent ORP vs. Perchlorate/Nitrate Destruction
Influent DO Range (0.5 - 1.2 mg/L)
ORP Measurement (mV)
Perchlorate/Nitrate Percent Destruction
Ethanol Reduction Testing
Date
Effluent ORP
Nitrate Removal
Perchlorate Removal


Ethanol Reactor Profiles
Influent DO Range (0.5 - 1.3 mg/L), 17% Recirculation
Ethanol Concentration (mg/L)
Undiluted GW (BS)
Reactor Influent (C)
1/4 h (D)
1/2 h (E)
3/4 h (F)
Reactor Effluent (G)
Position Along Reactor
1/29/98
2/4/98
2/6/98
2/17/98
2/18/98
2/20/98
Average



Conclusions

- Technology can treat low concentrations
- Treated water less than 4 ug/L perchlorate
- Treated water less than 0.1 mg/L nitrate
- Alternative microorganisms work
- Effluent could be potable with disinfection and filtration

Additional Conclusions

- Observed preference for nitrate
- Ethanol input optimized to support growth but not detected in produced water
- Minimum phosphorus required
- Operating controls - redox potential and DO
- Retention time - adjusted by equipment configuration and recycle
- No VOC reduction products detected

Phase 2 Treatability Study

- La Puente Valley County Water District
- Engineering data for scale up
- Rate between 500 and 1,000 gpm
- Disinfection
- Filtration
- Design in Summer 1998
- Startup in early 1999

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- Mike Girard - Aerojet
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  e-mail michael.girard@aerojet.com

Sun Liang
Metropolitan Water District
Southern California

Sun Liang is a Senior Engineer with the Metropolitan Water District of Southern California, where he has worked for more than 12 years. Currently, he is in charge of the Engineering Liaison Section in the Water Quality Division. Dr. Liang holds a BS degree in agricultural engineering from National Taiwan University, an MS degree in civil engineering from University of California at Berkeley, and a Ph.D. in civil and environmental engineering from the University of Michigan, Ann Arbor.

Dr. Liang has been conducting research in the field of water and wastewater treatment technologies for 20 years. He has extensive experience in conducting and supervising bench-, pilot-, and full-scale testing of water treatment processes for addressing water quality issues with particular emphasis on the treatment plant design and operation. His research encompasses studies on control of trace contaminants in drinking water with advanced water treatment processes such as membranes, ion exchange, and advanced oxidation processes, compliance with the Safe Drinking Water Act and all related regulations, occurrence and control of disinfection by-products, removal of trace organic compounds using activated carbon, optimization of water treatment processes for arsenic, natural organic matter, particulate, and pathogen removals, control of water quality in the distribution systems, and seawater desalination. Dr. Liang has been published more than 30 papers in the field of water treatment technologies.

Perchlorate Treatment by Enhanced Coagulation, Oxidation, and Membranes

Sun Liang, Ph.D., Karen Scott,
Leslie Palencia, and Jeanne-Marie Bruno
The Metropolitan Water District of Southern California

Objectives

- Investigate enhanced coagulation for ClO_4^- removal
- Investigate ClO_4^- removal in ozone/PEROXONE/GAC systems
- Evaluate the effectiveness of membranes for ClO_4^- reduction

Enhanced Coagulation Study Objectives

- Investigate the feasibility of enhanced coagulation for ClO_4^- removal
- Evaluate the effects of pH on enhanced coagulation for ClO_4^- removal

Experimental Design for Enhanced Coagulation

- Conventional treatment processes
- Chemical Dosages
  - 40 mg/L of Alum, 3 mg/L of polymer, 0.01 mg/L of filter aid
  - 25 mg/L of $FeCl_3$, 3 mg/L of polymer
- pHs at ambient and 6.5

Results from Enhanced Coagulation

Coagulant/ Dose (mg/L)	Filter Aid (mg/L)	Site	pH (unit)	CLO_4^- (μg/L)
$FeCl_3$/25	0	PI FE	8.28 7.24	6 7
$FeCl_3$/25	0	PI FE	8.27 7.05	7 6
Alum/40	0.01	PI FE	8.26 7.33	7 6
Alum/40	0.01	PI FE	8.21 6.65	7 7

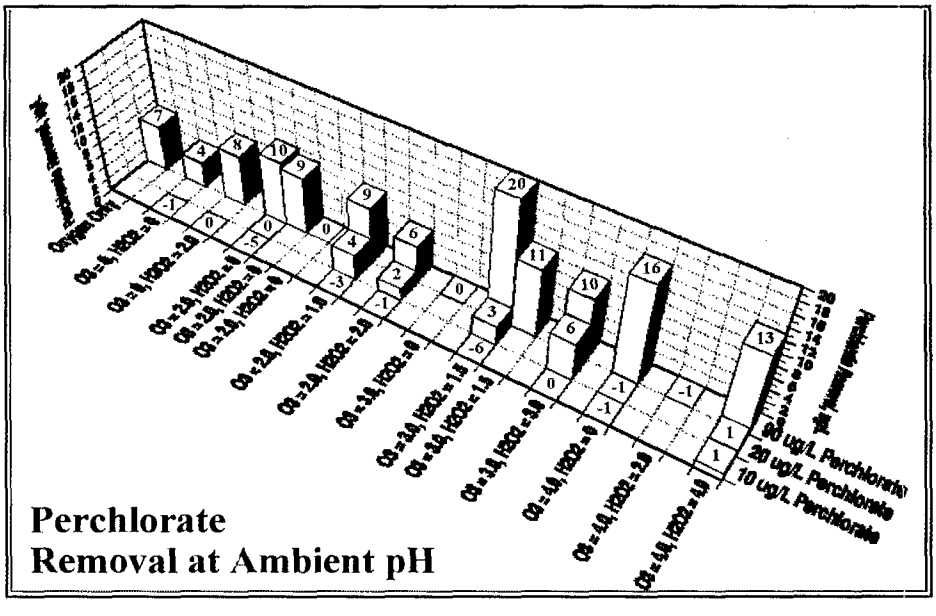
All tests with 3 mg/L of polyDADMAC polymer

Oxidation Study Objectives

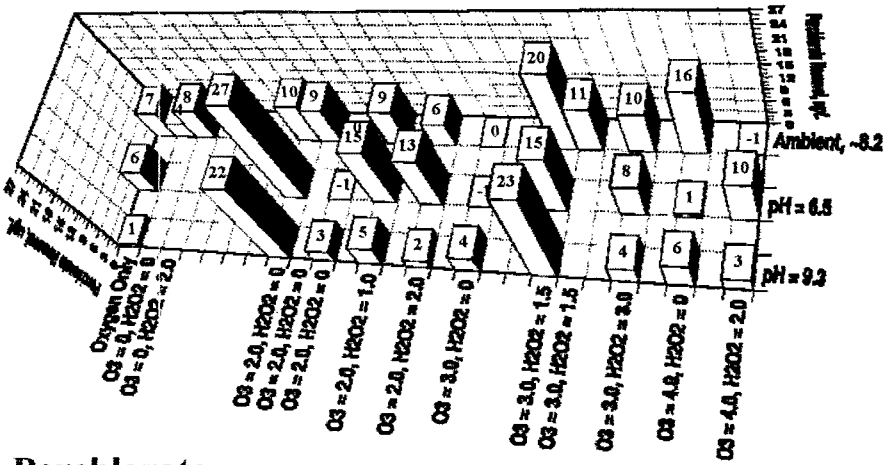
- Determine optimum applied ozone and/or hydrogen peroxide doses for ClO_4^- removal
- Identify the effects of various ClO_4^- levels on ClO_4^- removal
- Evaluate oxidation followed by GAC adsorption for ClO_4^- removal

Experimental Design for Oxidation

- Pilot plant flow of 3 gpm CRW through ozone contactor columns
- Applied ozone doses of 2, 3, and 4 mg/L without H_2O_2 and at 1:0.5 and 1:1 O_3:H_2O_2 ratios
- Spiked ClO_4^- at 10, 20, and 90 μg/L
- Tested ClO_4^- removal at ambient, 6.5, and 9.3 pH



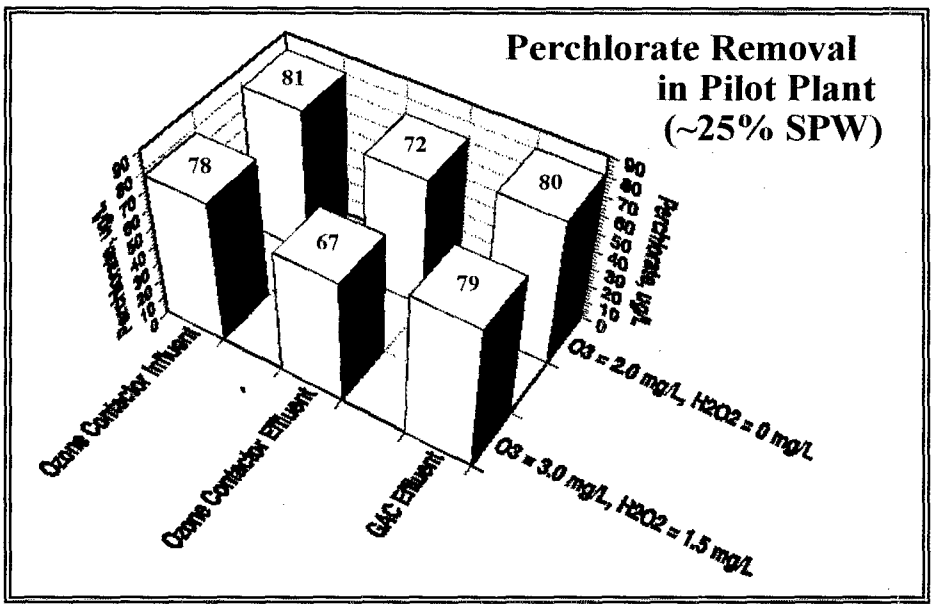
Perchlorate Removal at Ambient pH



Perchlorate
Oxidation at Various pHs (Dose = 90 µg/L ClO4)

Experimental Design for Oxidation/GAC

- Ozone contactor effluent treated in GAC mini column (82 mL/min)
- 2 conditions @ 90 mg/L ClO_4^- dose
  - 2 mg/L Ozone
  - 3 mg/L Ozone: 1.5 mg/L H_2O_2



Membrane Study Objectives

- Compare ClO_4^- removal using nanofiltration (NF) and reverse osmosis (RO) membranes
- Evaluate the effect of ClO_4^- feed concentration on ClO_4^- rejection rates
- Evaluate the effect of recycling the retentate

Experimental Design for Membranes

- Spiral Wound Membranes
  - Film Tech N70 4040-B (NF)
  - Fluid Systems TFC 4820-ULPT (RO)
- Post treatment
- Spiked ClO_4^- Dosages:
  - Low: 20-50 μg/L
  - Medium: 500-800 μg/L
  - High: 1,000-2,000 μg/L

Experimental Design (Cont'd)

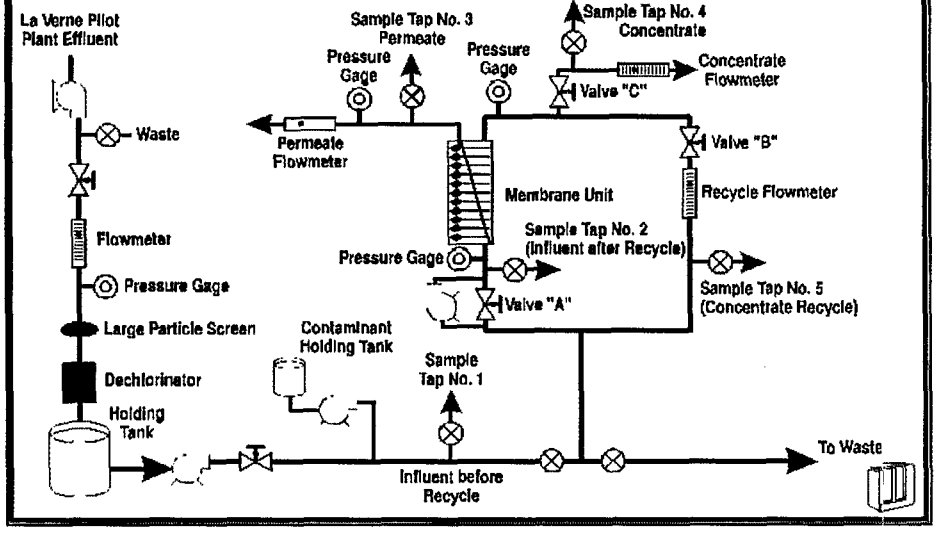
- Brine recycle at 50% of influent flow
- Test duration 3 hours
- Sampled 2nd and 3rd hour at influent, influent with recycle, permeate, and brine
- Measured ClO_4^-, total organic carbon (TOC), conductivity, UV_{254} absorbing organics, turbidity, and particle counts

Membrane Characteristics

Type	MWCO	Surface Charge	Compo-sition	Surface area (ft^2)	Flux (GFD)	Recovery (%)
NF	300 Da	Negative Charge	Thin Film Composite	82	15	20
RO	----	Negative Charge	Thin Film Composite	72	15	20

MWCO - molecular weight cutoff

Schematic of Membrane Bench Testing Unit

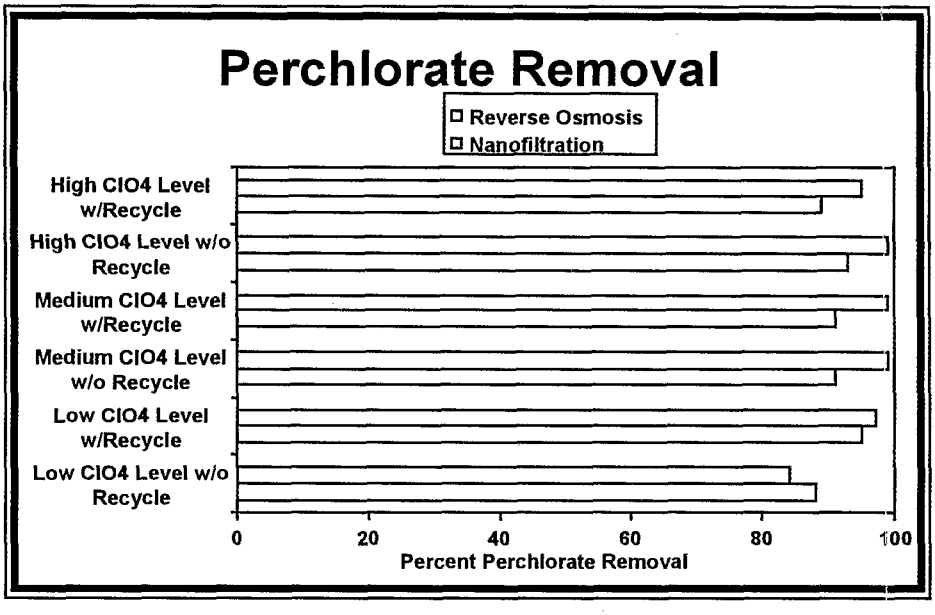


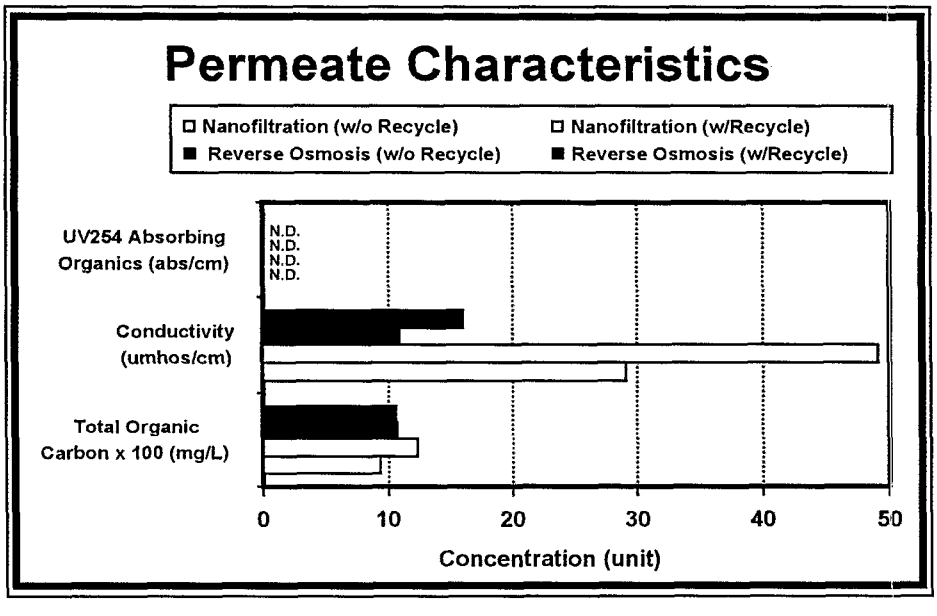
Membrane Influent Water Quality

Source Water	CRW
Total Organic Carbon	2.40 - 3.05 mg/L
UVA_{254}	0.024 - 0.032 abs/cm
Conductivity	969 - 1030 μmhos/cm
Temperature	20.4 - 21.5 $^{\circ}$C
pH	8.09 - 8.24
Turbidity	0.12 - 0.78 NTU
Particle Count	113 - 1590 /mL

Specific Flux for Membranes

Membrane	Average Pressure (psi)	Average Permeate (gpm)	Average Flux (GFD)	Specific Flux (GFD/psi)
NF	87	0.86	15	0.17
RO	106	0.76	15	0.14


Perchlorate Removal
Reverse Osmosis
Nanofiltration
High ClO4 Level w/Recycle
High ClO4 Level w/o Recycle
Medium ClO4 Level w/Recycle
Medium ClO4 Level w/o Recycle
Low ClO4 Level w/Recycle
Low ClO4 Level w/o Recycle
0
20
40
60
80
100
Percent Perchlorate Removal


Permeate Characteristics
Nanofiltration (w/o Recycle)
Nanofiltration (w/Recycle)
Reverse Osmosis (w/o Recycle)
Reverse Osmosis (w/Recycle)
UV254 Absorbing Organics (abs/cm)
N.D.
N.D.
N.D.
N.D.
Conductivity (umhos/cm)
Total Organic Carbon x 100 (mg/L)
0
10
20
30
40
50
Concentration (unit)

Brine Characteristics

- Perchlorate, TOC, conductivity, UV_{254} absorbing organics were concentrated in the brine
- Membrane systems concentrated ClO_4^- in brine by approximately 20-50 percent

Membrane Study Results

- NF and RO membranes can effectively remove ClO_4^- from CRW
- NF and RO performed equally well for ClO_4^- removal at low levels of ClO_4^- and lowered ClO_4^- concentration below 4 μg/L in permeate
- RO performed better than NF for ClO_4^- removal at medium and high levels of perchlorate

Membrane Study Results (Cont'd)

- Brine recycle did not significantly affect ClO_4^- percent rejection, but produced higher ClO_4^- levels in permeate
- Conductivity increased in permeate when brine recycled
- Brine disposal/treatment is required

Conclusions

- Enhanced coagulation does not appear promising in the treatment of ClO_4^- in CRW
- Oxidation does not appear promsing in treating low levels of ClO_4^- (10-20 μg/L); at higher levels (90 μg/L), some ClO_4^- removal may be expected, however results are mixed

Conclusions (Cont'd)

- Oxidation followed by GAC did not reduce ClO_4^- levels
- NF and RO membranes consistently removed greater than 80 percent of the applied ClO_4^-

Future
Perchlorate Treatment Studies

Frank J. Blaha, P.E.
AWWA Research Foundation
May 20, 1998

Organizational Background

- American Water Works Association Research Foundation
- In existence since 1965
- Most active since about 1984
- AWWARF Charter
- Related to but separate from AWWA
- AWWA created in 1881
- AWWA Charter
- Perchlorate brought to Foundation's attention in June 1997
- California water utilities concerned about impact
- AWWARF BOT approved limited involvement in June 1997

Treatment Project Background

- Variety of treatment methods needed
- Address concentrations in utility source waters
- Treat to less than detection limit/4 PPB

Perchlorate Research Program

- Most of 1998 work will be funded from a $2,000,000 Congressional earmark
- Congressman Jerry Lewis of California was the champion for obtaining this earmark
- Earmark for treatment-related research
- Funding to go to East Valley Water District (EVWD)
- EVWD in turn working with AWWARF to manage the research

EVWD/AWWARF
Issue Group Meeting

- Held in anticipation of the Congressional earmark
- Held in fall of 1997, in Ontario, California
- Issue Group: Workshop to Develop a Multiyear Research Plan
- Focused on treatment and analytical methodology research needs
- Funded by
  - EVWD
  - Main San Gabriel Basin Watermaster
  - Metropolitan Water District of Southern California
  - San Bernardino Valley Municipal Water District
  - Southern Nevada Water Authority

EVWD/AWWARF
Issue Group Meeting, *continued*

- Twenty-seven participants
  - Stakeholders
  - Experts in potential treatment technologies
  - Experts in analytical issues for perchlorate
- Addressed status of the problem, discussed issues
- Identified relevant research needs
- Broke up into small working groups to define individual projects

Planned 1998 Activities and Schedule

- **Five treatment-related projects moving forward**
  - Application of Bioreactor Systems to Low-Concentration Perchlorate Contaminated Water
  - Treatability of Perchlorate-Containing Waters by Reverse Osmosis and Nanofiltration
  - Treatability of Perchlorate Using Ion Exchange Technology
  - Removal of Perchlorate and Bromate in Conventional Ozone/GAC Systems
  - Investigation of Methods for Perchlorate Destruction in Aqueous Waste Streams

Planned 1998 Activities and Schedule, *continued*

- **Two analytically-related projects advertised**
  - Survey the Performance of the California DHS (Ion Chromatography) Analytical Protocol
  - Short Term Perchlorate Laboratory Issues
  - No proposals received

Planned 1998 Activities and Schedule, *continued*

- Treatment projects have Phased scope
- Intent for realistic/applied projects
- Known conditions
- Phase 1: Laboratory/Bench scale
- Phase 2: Pilot scale
- General Phase 2 work in proposals
- Pilot scale specifics identified end Phase I
- Phase 2 on Crafton-Redlands Plume - Terms of Congressional earmark

Planned 1998 Activities and Schedule, *continued*

- Winning proposal by mid-June
- Contracts completed 4 to 8 weeks after mid-June
- Probably August/September before work
- Timetable contingent on EPA grant released to EVWD
- Many responding teams include both universities and consulting firms

AWWARF Process

- During project period the investigator makes periodic reports of project progress to AWWARF and the Project Advisory Committee (PAC)
- PAC identified for all projects
- PACs are volunteer technical expert reviewers
- The PAC provides ongoing peer review on a project from drafting of the RFP through the final report
- Perchlorate treatment projects will also be peer reviewed by EVWD

Session #5/Treatment Technology

Distributed as a handout to participants at the Perchlorate Stakeholders Forum, held May 19-21, 1998 in Henderson, Nevada. Speaker: Frank Blaha, American Water Works Association Research Foundation.

Proposed Research Projects Developed by the Perchlorate Issue Group September 30-October 2, 1997

Group	Project Title	Project Number	Priority Ranking	$ 1,000s 1998	$ 1,000s 1999	$ 1,000s 2000	$ 1,000s 2001
Treatment	Application of Bioreactor Systems to Low-concentration Perchlorate Contaminated Water	1	1	688		320	
Treatment	Treatability of Perchlorate-Containing Waters by Reverse Osmosis and Nanofiltration	4	1	312		513	
Treatment	The Treatability of Perchlorate in Groundwater Using Ion Exchange Technology	9	1	312		513	
Analytical Methods	Survey the Performance of the California DHS (Ion Chromatography) Analytical Protocol	10	1	94			
Analytical Methods	Short Term Perchlorate Laboratory Issues	13	1	125			
Treatment	Removal of Perchlorate and Bromate in Conventional Ozone/GAC Systems	6	2	188	577		
Treatment	Investigation of Methods for Perchlorate Destruction in Aqueous Waste Streams	7	2	250		577	
Treatment	Assessment of Enzyme Based Reactor Systems on Perchlorate Reduction	2	3		385		1,090
Treatment	Literature/Expert Panel Review for Effective In-situ Treatment Technologies for Treatment of Perchlorate in Soil and Groundwater	3	3	63			
Treatment	Demonstration of Electrodialysis and Electrodialysis Reversal as a Control Technology for Perchlorate-Containing Waters	5	3		577		
Treatment	Investigation of Innovative Technologies for Perchlorate Removal from Drinking Water Sources	8	3		385	577	
Analytical Methods	Development of an Alternative Analytical Method for Measuring Perchlorate Ion at the 4 PPB Level	11	3			160	
Analytical Methods	Inter-Laboratory Study for the Performance Evaluation of the Cal-DHS Method: Determination of Perchlorate by IC	12	3		128		
Occurrence	Fate and Transport of Perchlorate in Drinking Water Sources	14	3	250	256		
Health Effects	Assess the Current Regional Health Effects Associated with Perchlorate in Ground and Surface Water Supplies	17	3		513	577	
	TOTAL			2,282	2,821	3,237	1,090

1 - Higher Priority Projects
2 - Medium Priority Projects
3 - Lower Priority Projects